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# JOURNAL

OF

## THE CHEMICAL SOCIETY.

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TRANSACTIONS.

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I.—*The Estimation of Methyl Alcohol in presence of Ethyl Alcohol.*

By THOMAS EDWARD THORPE, C.B., F.R.S., and JOHN HOLMES.

It is well known that when methyl and ethyl alcohols are treated with a mixture of potassium dichromate and sulphuric acid, the nature of the reaction and the character and relative quantity of the products vary with the conditions under which the process is conducted. Under one special set of conditions, ethyl alcohol furnishes a mixture of aldehyde, acetic acid, and acetal, whereas methyl alcohol under similar circumstances gives rise to formic acid and methylal (Trillat, *Compt. rend.*, 1898, 127, 232—234).

If, however, ethyl alcohol in aqueous solution is digested for a sufficient length of time with a mixture of potassium dichromate and sulphuric acid in a closed vessel at 100°, it furnishes very nearly its theoretical equivalent of acetic acid. Frankland and Frew (*Trans.*, 1891, 59, 93), found that 1 part by weight of ethyl alcohol furnished 1.281 parts of acetic acid, the theoretical amount being 1.305.

The same result follows if the dilute ethyl alcohol is treated in the cold with the oxidising mixture in quantity sufficient to oxidise it to acetic acid, and is then subsequently boiled with an additional amount of the same mixture.

Direct experiments have shown that the process of oxidation of the ethyl alcohol under these circumstances is always accompanied by the

liberation of a small quantity of carbon dioxide in amount equivalent to 0·5 per cent. of alcohol.

It is possible that the slight difference between the observed and calculated amounts of acetic acid observed by Frankland and Frew may be due to this cause.

It will be noticed that the amount of carbon dioxide formed is relatively very small—so small indeed that we were inclined at first to attribute it to some constant impurity in the alcohol rather than to a normal change under the influence of the oxidising mixture. We find, however, that it is invariably formed, no matter what may have been the origin of the alcohol employed. It is yielded by carefully dehydrated alcohol, however frequently it may have been redistilled, or apparently however much it may have been fractionated. We have experimented with a number of samples of the rectified spirits of commerce obtained on the large scale from a great variety of materials, for example, malt, maize, molasses, rye, &c., and such alcohol, after rectification, invariably gives practically the same relative amount of carbon dioxide, that is an amount directly proportionate to the quantity of alcohol which is being oxidised. Alcohol recovered from medicinal tinctures, or from cognac, rum, gin, sherry, or beer, after rectification, behaves in exactly the same way. No variation in the relative amount was noticed when the proportions of alcohol, potassium dichromate and sulphuric acid were considerably altered. The acetic acid formed by the oxidation, and recovered by distillation, when again treated with the same quantities of oxidising materials, gave no further evolution of carbon dioxide.

The amount of carbon dioxide formed is not affected by a preliminary boiling with caustic potash, or by distilling the alcohol from an acid solution, or by treating it with sulphurous or nitrous acid or bromine, or by the action of iodine in presence of an alkali.

It is unnecessary to set out here the details of these experiments, some 40 in number. The inference we draw from them is that the formation of the carbon dioxide is a constant and necessary product of the chemical change, and that under the conditions of oxidation employed by us the quantity formed is directly proportionate to the amount of ethyl alcohol present.

The main result as regards ethyl alcohol may be stated thus:—that under the conditions of oxidation employed, a minute quantity, not exceeding 0·5 per cent., of the alcohol undergoing oxidation is transformed into carbon dioxide, the remainder being converted into acetic acid.

In the case of methyl alcohol, the results are altogether dissimilar. No formic acid is produced—at least as an ultimate product—but the methyl alcohol is wholly decomposed into carbon dioxide and water.

The following experiments may be cited in proof of this: a sample of methyl alcohol, boiling between  $64.9^{\circ}$  and  $65.2^{\circ}$  and having a sp. gr. 0.7992 at  $15.5^{\circ}/15.5^{\circ}$ , was mixed with water in such proportion that 50 c.c. of the mixture contained 1.0118 grams of methyl alcohol. Fifty c.c. of the mixture were placed in a 300 c.c. flask, which could be closed with a ground-in stopper, and which was fitted with a funnel and side-tube; 10 grams of potassium dichromate and 25 c.c. of dilute sulphuric acid (1:4) were added, and the mixture allowed to remain for 18 hours. A further quantity of 10 grams of potassium dichromate and 50 c.c. of sulphuric acid mixed with an equal volume of water was added, and the contents of the flask heated to the boiling point for about 10 minutes, the evolved carbon dioxide being swept out of the apparatus by a current of air and collected in weighed soda-lime tubes. Two experiments gave 1.3810 and 1.3854 grams of carbon dioxide, equivalent to 99.4 and 99.7 per cent. of methyl alcohol respectively.

This difference in the behaviour of the two alcohols has already been made the basis of a method of examining whisky and other spirits for methylated spirit. Dupré (*Analyst*, 1876, 1, 4. Compare also Thudichum and Dupré, *Origin, Nature, and Use of Wine*, p. 205) has made use of the fact that ethyl alcohol may be converted into acetic acid by means of a mixture of potassium dichromate and sulphuric acid as a means of determining the actual amount of ethyl alcohol in a mixture of ethyl and methyl alcohols, and of thereby inferring the amount of admixed methyl alcohol. Dupré's method was examined by Hehner (*Analyst*, 1887, 12, 25), who preferred to measure the quantity of dichromate reduced instead of the acetic acid formed.

In the present communication, we describe a method of estimating methyl alcohol in presence of ethyl alcohol based on the determination of the amount of carbon dioxide evolved in the process of oxidation.

The process is as follows: the sample is mixed with water in such proportion that 50 c.c. of the mixture shall contain not more than 1 gram of methyl alcohol, and in the presence of ethyl alcohol not more than 4 grams of the mixed alcohols. Fifty c.c. of this mixture are then introduced into the oxidation flask, 20 grams of potassium dichromate and 80 c.c. of dilute sulphuric acid (1:4) added, and the mixture allowed to remain for 18 hours. A further quantity of 10 grams of potassium dichromate and 50 c.c. of sulphuric acid mixed with an equal volume of water are now added, and the operation conducted as already described.

When ethyl alcohol is present, a subtractive correction must be applied to the weight of carbon dioxide thus obtained, in the proportion of 0.01 gram of carbon dioxide for each gram of ethyl alcohol present.

The relative densities of the two alcohols being almost identical, the same table of densities can be used, with a sufficient approximation to accuracy, for the determination of the aggregate quantity of the two alcohols present.

As evidence of the trustworthiness of the method, the following results of a series of determinations on mixtures of methyl and ethyl alcohols in known proportions may be given.

*Percentage of Methyl Alcohol.*

Present...	9.0	9.0	8.0	6.9	5.6	4.8	2.5	1.0
Found ...	8.8	9.0	7.9	6.8	5.5	4.6	2.5	1.0

Ordinary methylated spirits must, according to law, consist of a mixture of plain or unsweetened spirits with one-ninth of their volume of wood naphtha.

It is required that the wood naphtha used for denaturing spirits shall contain at least 72 per cent. of methyl alcohol; that it shall not contain more than a certain proportion of aldehyde, acetone, and higher ketones, estimated as acetone by Messinger's method, nor more than a certain proportion of esters estimated as methyl acetate by hydrolysis; that it shall behave in a certain manner with an aqueous solution of bromine, and that it shall have a certain alkalinity.

The wood naphtha which is now used by methylators is fairly uniform in character as regards its content of methyl alcohol; thus, of 936 samples of wood naphtha which passed through the Government Laboratory during the year ending March 31st, 1903, 47 per cent. was found to contain between 72 and 75 per cent. of methyl alcohol, and 52 per cent. to contain between 75 and 80 per cent. of this alcohol by volume. The quantity of acetone and the higher ketones varied from 3.5 to 14 per cent., and the esters, mainly methyl acetate, ranged from 0.2 to 4 per cent. In addition, there were small quantities of unsaturated alcohols, amines, and other nitrogenous basic substances.

As regards the behaviour towards the oxidising solution of the substances other than methyl alcohol which may be present in wood naphtha, it is found that, on heating, ordinary acetone is almost wholly converted into acetic acid and carbon dioxide. In the cold, as with ethyl ether, no action occurs even after a long interval. Methyl acetate, in like manner, yields its theoretical equivalent of carbon dioxide and acetic acid. Allyl alcohol is wholly broken down, yielding carbon dioxide. Pyridine is not changed.

By experiments made with synthetically prepared mixtures, that is,

mixtures containing known amounts of ethyl and methyl alcohols mixed with known quantities of acetone, methyl acetate, allyl alcohol, and pyridine, it was found that the amount of carbon dioxide evolved corresponded closely with that theoretically producible. Thus, rectified spirits, to which was added one-ninth of its volume of a mixture consisting of :—

Methyl alcohol	80.6 per cent.	Allyl alcohol	0.2 per cent.
Acetone .....	14.0 „	Pyridine ...	0.2 „
Methyl acetate	5.0 „		

gave on oxidation 10.51 grams of carbon dioxide, as against a theoretical yield of 10.61 grams of carbon dioxide per 100 c.c. of the mixture.

From the circumstance that the wood naphtha now employed for methylation is of much more uniform quality than that formerly used, it is possible to ascertain, with a considerable approximation to accuracy, whether a sample of methylated spirits does actually contain its statutory quantity of wood naphtha, and also what is the amount of methylated spirits which may be present in a mixture of methylated spirits and ordinary spirits of wine.

It is obvious that the results, and therefore the inference to be drawn from them, may be affected to a slight extent by the circumstance that the substances commonly associated with the methyl alcohol in wood naphtha may be present in variable amounts. The difficulty due to this circumstance may, however, be largely removed by first treating the methylated spirits with light petroleum in the manner described in our recent communication (*Trans.*, 1903, **83**, 314), and then estimating the amount of carbon dioxide afforded by oxidising the distilled spirit.

Estimations made in this manner on synthetically prepared mixtures containing these substances in quantities varying from the highest to the lowest percentages commonly found in wood naphtha afforded the following results :

*Percentage of Methyl Alcohol.*

Present .....	8.0	8.0	7.5
Found .....	8.3	8.3	7.8

The slight increase in the amount found as compared with that known to be present is due to the circumstance that small quantities of acetone equal to 0.5 per cent. of this ketone are not extracted by the light petroleum ; this residue furnishes carbon dioxide equivalent to 0.3 per cent. of methyl alcohol by volume.

A similar result was obtained on submitting a mixture of the two alcohols with acetone to the above treatment.

Estimations were then made on methylated spirits prepared with samples of commercial wood naphtha, in which the ketones, esters, and other substances had been determined by the methods already referred to, and the following results were obtained :

*Percentage of Methyl Alcohol.*

(1) Found .....	8.3	8.1	7.9
(2) Calculated .....	8.3	8.3	7.8

Series (1) gives the corrected results obtained after treatment by the petroleum method, whilst series (2) gives the calculated results obtained by deducting in each case the amount of carbon dioxide theoretically producible from the quantities of ethyl alcohol, acetone, methyl acetate, &c., present, as determined by experiment, from the total amount of carbon dioxide yielded by the direct oxidation of the sample.

A general method for ascertaining whether tinctures or other medicinal preparations contain methylated spirits, and to what extent, is as follows : the spirit from 25 c.c. of the sample, or from 50 c.c. if it contains less than 50 per cent. of alcohol, is treated with light petroleum to remove essential oils, &c., in the manner described in our recent communication (*loc. cit.*), and then distilled and diluted with water to a volume of 250 c.c. ; 50 c.c. of this mixture are then oxidised with 20 grams of potassium dichromate and 80 c.c. of dilute sulphuric acid (1 : 4), and further treated as already described in this communication.

If the weight of carbon dioxide thus obtained does not exceed 0.01 gram for each gram of alcohol present, this amount being equivalent to 0.7 vol. of methyl alcohol in 100 vols. of the alcohol, then it may be concluded that the sample contains only spirits of wine.

Should the weight of carbon dioxide exceed this amount, its equivalent in methyl alcohol by volume must be subjected to a subtractive correction of from 0.7 to 1 per cent. (depending on the amount of methylated spirits present), the percentage of methylated spirits being calculated on the assumption that the quantity of methyl alcohol occurring in dehydrated methylated spirit does not exceed 8.8 per cent.

## II.—*Halogen Derivatives of Diphenyl and Dihydroxydiphenyl.*

By JOHN CANNELL CAIN.

In an investigation on the action of water on the diazonium salt prepared from 3:3'-dichlorobenzidine (Trans., 1903, 83, 688), only a very small quantity of 3:3'-dichloro-4:4'-dihydroxydiphenyl was obtained, the chief product being of a quinonoid nature. It appeared, therefore, of interest to study the behaviour of this diazonium salt when subjected to the processes employed in replacing the diazo-groups by hydrogen, chlorine, bromine, iodine, cyanogen, and carboxyl radicles.

A very convenient method of preparing 3:3'-dichloro-4:4'-dihydroxydiphenyl has been devised, which consists in chlorinating 4:4'-dihydroxydiphenyl in glacial acetic acid solution with the calculated quantity of chlorine. In connection with this part of the work, both the monochloro- and the trichloro- derivatives were prepared, the limit of the chlorination being the tetrachloro-compound, which has already been described by Magatti (*Bér.*, 1880, 13, 224).

### EXPERIMENTAL.

#### 3:3'-Dichlorodiphenyl.

3:3'-Dichlorobenzidine (25 grams) was dissolved in ethyl alcohol, a mixture of strong sulphuric acid and alcohol added, and then, after cooling, a slight excess of dry sodium nitrite. The alcoholic solution of the diazonium sulphate thus obtained was boiled for half an hour, the alcohol evaporated off, and the residue distilled in a current of steam. The easily fusible yellowish-white solid collecting in the distillate was recrystallised from dilute alcohol. The 3:3'-dichlorodiphenyl thus obtained crystallises from dilute alcohol in white needles and is easily soluble in ether, alcohol, and benzene; it melts at 29° and boils at 298°.

0.1789 gave 0.2308 AgCl. Cl = 31.9.

$C_{12}H_8Cl_2$  requires Cl = 31.8 per cent.

#### 3:4:3':4'-Tetrachlorodiphenyl.

3:3'-Dichlorobenzidine (12.7 grams) was dissolved in 90 c.c. of hydrochloric acid of sp. gr. 1.16, diluted with 45 c.c. of water, the solution being cooled and diazotised with 6.9 grams of sodium nitrite dissolved

in a very small quantity of water. The resulting brownish-yellow solution was filtered and added to copper powder (the "copper bronze" of commerce) which had been moistened with hydrochloric acid. Nitrogen was immediately evolved, and on the following day the mixture was filtered and extracted with ether. After evaporating off the solvent from the extract, the dry residue was distilled under diminished pressure, and by this means the tetrachlorodiphenyl was freed from a red by-product. The solid distillate was crystallised twice from glacial acetic acid, from which it separates in fine white needles, melting at  $172^{\circ}$  and boiling at  $230^{\circ}$  under 50 mm. pressure. The tetrachlorodiphenyl thus obtained dissolves easily in ether, alcohol, or benzene.

0.1392 gave 0.2741 AgCl. Cl = 48.70.

$C_{12}H_6Cl_4$  requires Cl = 48.58 per cent.

*3 : 3'-Dichloro-4 : 4'-dibromodiphenyl.*

3 : 3'-Dichlorobenzidine (12.7 grams) was diazotised as in the preceding case, except that sulphuric acid was used instead of the hydrochloric acid; the filtered solution was poured into a solution of 20 grams of potassium bromide, to which copper powder had been added. The mixture was left for a time, then filtered, and extracted with ether. The red residue obtained after removing the solvent was distilled under diminished pressure. The dichlorodibromodiphenyl, which is soluble in the ordinary organic solvents, on crystallisation from glacial acetic acid separated in white needles melting at  $176-177^{\circ}$ .

0.1784 gave 0.2969 AgCl + AgBr. Halogen = 60.89

$C_{12}H_6Cl_2Br_2$  requires Cl + Br = 60.60 per cent.

*3 : 3'-Dichloro-4 : 4'-di-iododiphenyl.*

A solution of the diazonium sulphate was added to 20 grams of potassium iodide dissolved in water. Nitrogen was at once evolved, and after about 12 hours the mass was filtered, boiled with water to expel traces of free iodine, dried, and distilled under diminished pressure. The product was recrystallised from glacial acetic acid and obtained in pale yellow, fern-like aggregates of needles, melting at  $162^{\circ}$  and boiling at  $275^{\circ}$  under 10 mm. pressure; it is easily soluble in the ordinary organic solvents.

0.1552 gave 0.2448 AgCl + AgI. Halogen = 67.69.

$C_{12}H_6Cl_2I_2$  requires Cl + I = 68.39 per cent.

The effect of metallic sodium on the two foregoing substances was studied in the hope of obtaining a new condensation product, for

although Fittig has shown (*Annalen*, 1864, 132, 205) that this metal has no action on 4:4'-dibromodiphenyl, yet a 4:4'-dibromo- or 4:4'-di-iodo-diphenyl which contained a chlorine atom immediately adjacent to each atom of bromine or iodine might conceivably be more easily decomposed. Experiments were made in both ethereal and benzene solutions, but no action could be detected either with the dichlorodibromodiphenyl or the di-iodo-compound. These substances can even be heated with copper powder considerably above their melting points without any condensation taking place.

*The Nitrile of 3:3'-Dichlorodiphenyl-4:4'-dicarboxylic Acid*  
(3:3'-Dichloro-4:4'-dicyanodiphenyl).

A solution of the diazonium salt was added to a boiling solution of cuprous cyanide. After some time, the nitrile was collected, a small portion extracted with ether, the ethereal solution evaporated, and the red residue distilled. The red by-product was not volatile, and the nitrile was thus obtained as a white substance which crystallised from alcohol in white, flocculent needles melting at 152—153°.

*3:3'-Dichlorodiphenyl-4:4'-dicarboxylic Acid.*

The bulk of the crude nitrile was saponified by boiling with dilute caustic soda for a few hours. On filtering and acidifying, the acid separated out and was filtered, dried, and crystallised, first from glacial acetic acid and then from alcohol. From the latter solvent, it separates in small needles melting at 287—288°.

The substance thus obtained is very sparingly soluble in water, but dissolves more easily in alcohol or ether.

0.1280 gave 0.11753 AgCl.  $\text{Cl} = 22.71$ .

$\text{C}_{14}\text{H}_8\text{O}_4\text{Cl}_2$  requires  $\text{Cl} = 22.80$  per cent.

*Chlorination of 4:4'-Dihydroxydiphenyl.*

As already indicated, Magatti (*loc. cit.*) obtained a tetrachlorodiphenol by the complete chlorination of 4:4'-dihydroxydiphenyl ( $\gamma$ -diphenol) in acetic acid solution.

Schmidt and Schultz (*Annalen*, 1881, 207, 334), by treating  $\gamma$ -diphenol with phosphorus pentachloride, obtained three substances, namely, (1) a chlorinated diphenol (m. p. 126°); (2) *p*-dichlorodiphenyl (m. p. 148°); (3) pentachlorodiphenyl (m. p. 179°).

I have already shown that the first product was most probably not

a trichlorodiphenol as suggested by Schmidt and Schultz, but was identical with 3 : 3'-dichloro-4 : 4'-dihydroxydiphenyl (*loc. cit.*) These chemists, assuming that the first product is a trichloro-derivative, explain the formation of the third compound from it by the replacement of hydroxyl by chlorine.

By chlorinating  $\gamma$ -diphenol with bleaching powder solution in presence of acids, a deep violet coloration is produced, which was noticed by Schmidt and Schultz. If this operation is carried out quantitatively, the interesting fact is demonstrated that three molecular proportions of chlorine are absorbed by one of  $\gamma$ -diphenol.

The diphenol (1 gram) was dissolved in caustic soda, dilute sulphuric acid added to the solution, and a solution of bleaching powder introduced from a burette until a reaction was obtained with starch-iodide paper. The amount of chlorine used was 1.14 grams, this quantity being identical with that corresponding with three molecules of chlorine.

The reaction does not appear to go quite smoothly, as a pure substance could not be isolated from the product of chlorination, but analyses indicated that a trichlorodiphenyl had been formed.

The object of these experiments being to find a method of obtaining the dichlorophenol, the direct chlorination in acetic acid solution was studied, and it was found that the mono-, di-, and tri-chloro-derivatives could be prepared by taking calculated quantities of chlorine obtained by oxidising hydrochloric acid with a weighed amount of potassium dichromate.

### *3-Chloro-4 : 4'-dihydroxydiphenyl.*

The diphenol (1.86 grams) was dissolved in glacial acetic acid, and a current of dry chlorine, obtained by warming 0.98 gram of potassium bichromate with hydrochloric acid, was passed into the solution at the ordinary temperature. The gas was at once absorbed, and at the conclusion of the experiment the solution was concentrated to a small bulk and poured into water. The monochloro-compound, which was obtained as a white precipitate, was recrystallised from dilute acetic acid; it forms white needles, soluble in ether, alcohol, or benzene, and melting at 215°.

0.1628 gave 0.10463 AgCl. Cl = 15.89.

$C_{12}H_9O_2Cl$  requires Cl = 16.08 per cent.

### *3 : 3'-Dichloro-4 : 4'-dihydroxydiphenyl.*

The chlorination of the diphenol was carried out exactly as in the preceding case, except that twice the quantity of potassium dichromate was used.

The crude dichloro-compound was recrystallised from hot water and obtained in fine, white needles melting at  $124^{\circ}$ . Its properties were identical with those of the 3:3'-dichloro-4:4'-dihydroxydiphenyl (m. p.  $124^{\circ}$ ), obtained by another method (*loc. cit.*), and a mixture of the two preparations melted exactly at  $124^{\circ}$ . This identity is, of course, a proof of the constitution of this and the preceding substance.

0.1827 gave 0.20763 AgCl. Cl = 28.09.

$C_{12}H_8O_2Cl_2$  requires Cl = 27.81 per cent.

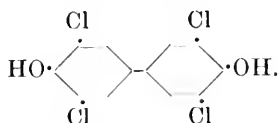
3:3':5(?)-Trichloro-4:4'-dihydroxydiphenyl.

This trichloro-derivative, produced by using the appropriate amount of potassium dichromate, was obtained from dilute acetic acid in white needles; it is soluble in ether, alcohol, or benzene, and melts at  $179^{\circ}$ .

0.0899 gave 0.13083 AgCl. Cl = 35.96.

$C_{12}H_7O_2Cl_3$  requires Cl = 36.75 per cent.

Although the orientation of the third atom of chlorine has not been absolutely demonstrated, yet there can be little doubt that the halogen occupies the position indicated by the notation used in naming the compound. The tetrachloro-compound, which was also prepared, and found to correspond exactly with the substance described by Magatti, has, in all probability, the following constitution:



My thanks are due to Messrs. Levinstein, Limited, Manchester, for a supply of the pure 3:3'-dichlorobenzidine, and to Messrs. K. Whitaker and J. Brothers, who assisted in carrying out certain portions of the practical work.

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### III.—*Separation and Estimation of Silver Cyanide and Silver Chloride.*

By ROBERT HENRY ADERS PLIMMER, D.Sc. (Grocers' Company's Research Student).

ON boiling a mixture of silver chloride and cyanide with dilute nitric acid, I noticed that the latter salt was easily dissolved with the evolution of hydrogen cyanide, and on collecting this gas in a solution of silver nitrate it was found that the amount of silver cyanide produced was constant. Further experiments showed that silver cyanide was quantitatively decomposed by the action of dilute boiling nitric acid, so that by this means it can be easily separated from silver chloride and estimated.

The earliest and most complete investigations on silver cyanide were made in 1844 by Glassford and Napier (*Phil. Mag.*, 25, 66), who state that nitric acid has no effect on silver cyanide except when concentrated and boiling, and that sulphuric acid diluted with its own volume of water decomposes silver cyanide, liberating hydrogen cyanide and forming silver sulphate; by this means, the cyanide may be separated from silver chloride, which remains unchanged. These observers did not, however, collect the hydrogen cyanide and determine its amount. This observation, although cited in Gmelin's Handbook, has apparently been overlooked, for other treatises on analytical chemistry give only two methods of separation depending on the decomposition of silver cyanide by acids. These processes are (1) that of Kraut (*Zeit. anal. Chem.*, 1863, 2, 243), which consists in oxidising silver cyanide with nitric acid (sp. gr. 1.2) in sealed tubes for several hours at 100° or for one hour at 150°, and (2) that described in Sonnenschein's *Handbuch der Analytischen Chemie* (1871, p. 252), which depends on the action of hydrochloric acid, whereby the silver cyanide is converted into silver chloride, the difference in weight indicating the quantity of cyanogen.

#### EXPERIMENTAL.

The first experiments were carried out with silver cyanide prepared from potassium cyanide in the usual way and dried at 100°. A known weight was gently boiled in a small flask with 200 c.c. of dilute nitric acid, the strength of which was about twice normal, the flask being connected with a condenser placed in a vertical position, to the end of which was attached a Volhard's receiver containing excess of silver

nitrate solution acidified with dilute nitric acid. The hydrogen cyanide passing over with the steam produced a white precipitate in the silver nitrate solution, but although after one hour the silver cyanide was almost entirely decomposed, yet a small quantity remained which was dissolved completely only after boiling for about two hours. This decrease in the rate of decomposition is in all probability due to the resistance offered by the hard lumps which are formed in drying the silver cyanide. The silver cyanide obtained in the receiver was weighed and indicated a loss of 8—10 milligrams; this deficiency was attributed to a small residue of silver chloride, the presence of which was due to the potassium chloride originally contained in the potassium cyanide under examination.

Experiments were then performed with silver cyanide prepared from hydrogen cyanide obtained by the action of dilute sulphuric acid on potassium ferrocyanide. Here, again, a slight loss amounting to about 1 per cent. occurred, as will be seen from the following results:

AgCN taken.*	AgCN obtained.	Loss.
0.3524	0.3484	0.0040
0.5042	0.4994	0.0048
0.3778	0.3744	0.0034
0.2484	0.2446	0.0038
0.3328	0.3288	0.0040

In every case, the silver cyanide at the commencement was rapidly attacked, but the last portions required prolonged boiling for 1—2 hours in order to complete the decomposition. During this time, the nitric acid, which at first was of normal strength, or, in some cases, even weaker, became more concentrated, but although this might have caused a slight oxidation of the silver cyanide, yet it seemed as if this loss were in a great measure due to experimental error, since a deficiency of almost the same amount occurred when the silver cyanide was dissolved in warm ammonia and reprecipitated with dilute nitric acid. Heat was applied in this case because the salt dissolved very slowly in the cold. Two experiments were made.

AgCN taken.	AgCN obtained.	Loss.
0.2590	0.2572	0.0018
0.3996	0.3954	0.0042

The amount of silver in the silver cyanide produced from the hydrogen cyanide obtained in the foregoing distillation was estimated with the following results:

\* The tabulated weights throughout are expressed in grams.

0.2952 AgCN gave 0.2376 Ag. Ag = 80.49 per cent.

0.3948 AgCN „ 0.3174 Ag. Ag = 80.39 „

AgCN requires Ag = 80.56 per cent.

The amount of silver in the silver cyanide reprecipitated from the ammonia solution was also estimated.

0.2484 AgCN gave 0.1996 Ag. Ag = 80.35 per cent.

0.3874 AgCN „ 0.3120 Ag. Ag = 80.54 „

Although dry silver cyanide can in this way only be directly estimated with an accuracy of about 1 per cent., it can be completely separated from silver chloride and indirectly estimated by difference. The following two results were obtained with a mixture of these compounds :

AgCN taken.	AgCN obtained.	Loss.	AgCl taken.	AgCl obtained.
0.3594	0.3552	0.0042	0.6970	0.6974
0.2624	0.2584	0.0040	0.2288	0.2290

From these experiments, it will be seen that it is not necessary to heat the mixture of silver cyanide and silver chloride in a sealed tube with concentrated nitric acid when their estimation is required.

Silver cyanide, however, when freshly precipitated and not dried, is quantitatively decomposed into prussic acid by the action of dilute nitric acid.

In these experiments, a 2 per cent. solution of potassium cyanide was used; in each case, 10 c.c. were allowed to flow from a burette into a known quantity of water containing 5 c.c. of a 10 per cent. solution of silver nitrate. This solution was then acidified with nitric acid until its strength in some experiments was normal, in others semi-normal, and distilled. The distillate, as in the previous experiments, after passing through a condenser was collected in a Volhard's receiver containing 5 c.c. of the solution of silver nitrate acidified with dilute nitric acid. The time taken to completely decompose the silver cyanide was from  $\frac{1}{2}$ — $\frac{3}{4}$  hour, but the distillation was continued for an hour so as to ensure that all the hydrogen cyanide had passed over. The silver cyanide obtained was collected on a tared filter paper, washed with cold water, dried at  $100^{\circ}$ , and weighed.

Two determinations of the amount of silver cyanide (+ silver chloride) given by 10 c.c. of the 2 per cent. solution of potassium cyanide directly were previously made with the following results :

10 c.c. KCN solution gave 0.3892 AgCN	} mean = 0.3887.
10 c.c. „ „ 0.3882 „	

The small residue of silver chloride which remained behind and which, as already mentioned, was due to traces of potassium chloride in the potassium cyanide, was neglected in the first two experiments, but in the remaining six estimations its weight was also determined. Ten c.c. of the foregoing potassium cyanide solution were employed in each experiment, and the results were as follows:

AgCN obtained.	Residue of AgCl.	Total.	Error	
0.3830	—	—	—	
0.3844	—	—	—	
0.3874	0.0038	0.3912	+ 0.0025	} mean = - 0.0004
0.3864	0.0044	0.3908	+ 0.0021	
0.3832	0.0044	0.3876	- 0.0011	
0.3826	0.0052	0.3878	- 0.0009	
0.3846	0.0010	0.3856	- 0.0031	
0.3844	0.0022	0.3866	- 0.0021	

The variations in the amount of silver cyanide obtained are in all probability due to the experimental errors incurred in measuring out the 10 c.c. from a burette, or in drying the tared filter papers at 100°.

A series of six experiments was also carried out with a mixture of freshly precipitated silver cyanide and silver chloride obtained by mixing 10 c.c. of a 2 per cent. potassium chloride solution with the same amount of the 2 per cent. potassium cyanide solution and 10 c.c. of aqueous silver nitrate, then acidifying with nitric acid, and distilling in the manner already described.

The amount of silver chloride given by the potassium chloride solution was estimated separately; two experiments with 10 c.c. yielded 0.3918 and 0.3912 gram of precipitate, giving a mean of 0.3915 gram.

Hence the total amount of insoluble silver salts obtainable from 10 c.c. of potassium cyanide solution and 10 c.c. of potassium chloride solution is 0.7802 gram.

The following table contains the results obtained with the mixture (KCN = 10 c.c.; KCl = 10 c.c.):

AgCN obtained.	AgCl obtained.	Total.	Error.	
0.3840	0.3910	0.7750	- 0.0052	} mean = - 0.0013
0.3842	0.3954	0.7796	- 0.0006	
0.3854	0.3922	0.7776	- 0.0026	
0.3854	0.3940	0.7794	- 0.0008	
0.3866	0.3946	0.7812	+ 0.0010	
0.3832	0.3974	0.7806	+ 0.0004	

The foregoing experiments show that by the action of hot dilute

nitric acid on a mixture of silver chloride and cyanide the latter compound may be entirely removed from the former and its amount directly estimated.

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#### IV.—*Action of Malt Diastase on Potato Starch Paste.*

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##### *Introductory.*

It is well known that when starch paste is hydrolysed by an aqueous solution of malt diastase, the speed of the reaction as indicated by the diminution of the specific rotatory power, and the increase of the cupric reducing power of the products in a given time becomes less the more the temperature of hydrolysis exceeds a certain point, which is termed the optimum temperature of diastatic action.

Brown and Heron (Trans., 1879, 35, 596) give numerous determinations of the specific rotatory power of the products of the hydrolysis of potato starch in the form of paste by malt extract at different temperatures after the lapse of definite intervals of time, and from their results it may be deduced that the optimum temperature of diastatic action lies between 50° and 60°. Kjeldahl, who, in the same year (*Compt. rend. labor. de Carlsberg, Copenhagen*, 2, 109), confirmed this conclusion by determinations of the cupric reducing powers of the products in question, found the optimum temperature to be 55°.

The velocity of the reaction between diastase and starch paste, if measured by the constants just referred to, becomes less, *pari passu*, at temperatures above 55° up to the point at which the activity of the enzyme is permanently destroyed. Moreover, if solutions of diastase are heated above 55° before mixing with starch paste, the same apparent slackening of the reaction or weakening of the enzyme is observed. The effect of heat on diastase is usually spoken of as restriction, a term we have adopted, it being understood that in all the experiments recorded in this paper the diastase was invariably previously heated in aqueous solution.

In a paper read before the Midland Counties Institute of Brewing (*J. Fed. Inst. Brewing*, 1902, 8, 475), we gave an account of a large number of experiments on the action of diastase (previously

heated in aqueous solution and in the dry state, at various temperatures for definite intervals of time) on potato starch paste.

In the case of previously heated diastase solutions, we found that when the temperature employed was not above the optimum point, the reaction with starch paste near the same temperature (not above it), provided a sufficient mass of the enzyme were employed, proceeded rapidly for the first 75 minutes, and then advanced steadily until, at the end of about 40 hours, the specific rotatory and cupric reducing powers of the product were approximately those of maltose. When, however, the diastase solution was previously heated above the optimum temperature, the reaction was not only slower, as has been observed by others, but the products were apparently different. Thus we found that by the action on starch paste of diastase solutions, restricted in this way at 70° (the hydrolysis being allowed to proceed at 55°), *d*-glucose could invariably be detected after the reaction had continued for several hours.

On the other hand, the products of the transformation of starch made with diastase solutions which had been previously heated for 30—60 minutes at temperatures not exceeding 55° were found by us not to contain *d*-glucose, even when the reaction was taken to its final stage. Nor could we detect *d*-glucose in the starch derivatives made with diastase, which had been previously heated in the dry state at temperatures as high as 125°. The only change in the enzyme observed in such cases was a weakening of its action.

It therefore appeared that the production of *d*-glucose was connected with the initial heating of the diastase solutions at temperatures above 55°, and since the publication of the earlier paper (*loc. cit.*) the work has been continued principally with the object of obtaining further information on this point.

The diastase used in the experiments was prepared by C. J. Lintner's method (*J. pr. Chem.*, 1886, ii, 34, 378), and, except where otherwise stated, from Odessa malt dried at a temperature not exceeding 33°.

We are indebted to Mr. R. E. Free, of Messrs. Free, Rodwell and Co., Mistley, for placing at our disposal several samples of this low-dried malt. The starch used was the purest potato farina. The temperature of hydrolysis never exceeded 55°, but in a few cases it was a degree or two lower than this.

The methods of analysis adopted are explained in our earlier paper (*loc. cit.*), with the exception of that used to estimate *d*-glucose, which consisted in weighing the phenylglucosazone produced under standard conditions, and calculating from the weight the percentage of the hexose on the total solid matter in the solution. The values obtained are denoted by the symbol  $G_{3-93}$ . The symbol  $R_{3-93}$  represents the

cupric reducing power, expressed as percentage of maltose on the total solid matter, calculated by the solution factor 3.93 from the specific gravity of the solution.

### EXPERIMENTAL.

In order to give some idea of the power of the diastase preparations employed, we may quote the following experiment from our earlier paper, in which unrestricted diastase from the same Odessa malt (0.08 gram) was allowed to act, at a temperature of 55°, on starch (10 grams) made into paste of about 3 per cent. concentration.

Time.	$[\alpha]_{D, 3.93}$	$R_{3.93}$
1 $\frac{1}{4}$ hours	150.0°	78.8
18 $\frac{1}{2}$ „	143.6	90.6
42 „	138.5	99.7
66 „	138.0	96.9
138 „	137.6	99.5

An experiment since carried out with diastase from the same source (0.5 gram) and starch (10 grams) made into a paste of about 2 per cent. concentration gave the following results, the hydrolysis being conducted at 47°:—

Time.	$[\alpha]_{D, 3.93}$	$R_{3.93}$
67 hours	135.5°	99.6
89 „	134.6	97.5

This solution, which gave well-defined maltosazone but no glucosazone on treatment with phenylhydrazine acetate, also yielded maltose in the crystalline form.

These experiments show that the reducing power attains a maximum and then undergoes diminution, a phenomenon which we have previously referred to as "reversion," but for which we have not at present found a satisfactory explanation. It is invariably exhibited in the case of conversions with both unrestricted and restricted diastase, and it may occur at any point of the reaction if the latter has stopped, because an insufficient amount of diastase is present to carry the hydrolysis to its final stage.

In addition to the cases already mentioned (*loc. cit.*), we have now obtained further evidence showing that not only does the reducing power diminish when the temperature of hydrolysis is maintained beyond a certain period, but that the rotatory power increases.

The following experiments were all made with diastase restricted by heating in aqueous solution at various temperatures.

## Series I.

A. Three separate amounts of diastase, (a) 1 gram, (b) 0.5 gram, (c) 0.2 gram, were restricted at 77.5—78° for an hour. They were then added to three 10 gram quantities of starch, each made into paste with 375 c.c. of water, and placed in a thermostat at 52—55°.

Time.	$[\alpha]_{D 3.93}$			$R_{3.93}$		
	(a).	(b).	(c).	(a).	(b).	(c).
43 hours	191.1°	190.9°	187.2°	6.7	2.6	1.7
91 „	184.5	191.4	189.7	15.3	4.4	5.8
187 „	181.7	191.1	189.4	18.7	4.5	5.4
259 „	183.2	—	—	20.8	—	—

(a), on fractionation, gave a dextrin insoluble in 46 per cent. alcohol having the constants  $[\alpha]_{D 3.93} = 184.0^\circ$ ,  $R_{3.93} = 2.36$ . A fraction soluble in 80 per cent. alcohol having a reducing power of  $R_{3.93} = 57.3$  was separated; but as this was contaminated with foreign matter from the diastase, and its amount was too small to attempt purification, it was not further examined; (b) and (c) were fractionated and found to contain no constituent capable of giving a crystalline phenylosazone:

B. An attempt was now made to carry this reaction further by employing a lower temperature of restriction. To this end, 0.5 gram of diastase was restricted for an hour at 75°, the solution being then added to 10 grams of starch made into paste with 375 c.c. of water. The temperature of hydrolysis was 52—55°.

Time.	$[\alpha]_{D 3.93}$	$R_{3.93}$
65 hours	171.8°	49.5
113 „	172.9	44.7
161 „	173.9	47.0
280 „	158.6	62.5

The reaction would have undoubtedly proceeded further if more diastase had been employed. The final solution, which gave no insoluble osazone, yielded a soluble osazone having the form of “iso-maltosazone” and melting below 150°. This result showed that *d*-glucose, if formed at all, had again disappeared (see pp. 25—27).

C. Diastase (2.25 grams) was restricted for 15 minutes at 74°, and subsequently for an hour at 75—75.5°. The solution was then added to a paste prepared from 30 grams of starch, and placed in a thermostat at 55°, the total volume of the liquid being 700 c.c.

Time.	$[\alpha]_{D 3.93}$	$R_{3.93}$
16 hours	191.0°	10.2
88 „	190.0	11.7
187 „	186.7	16.4

At the end of 187 hours, the solution still gave a blue coloration with iodine, and after adding 0.02 gram of unrestricted diastase it was again placed in the thermostat at 55°.

Time.	$[\alpha]_{D, 55^\circ}$	$R_{55^\circ}$
65 hours	138.9°	95.6
89   ,,	139.7	93.8

After 89 hours, the solution yielded a small amount of insoluble osazone, but the main portion of the product obtained by heating with phenylhydrazine was soluble in hot water, and had the form of "iso-maltosazone."

Subsequent experiments showed that the period of heating at 75° was too long, and that the unrestricted diastase subsequently added was not in sufficient quantity to complete the reaction. Any *d*-glucose which might have been formed would probably have disappeared again.

#### Series II.

The diastase (1.432 grams) was restricted at 75° for an hour, the solution filtered and added to 10 grams of starch made into a paste with water, the total volume being 400 c.c. After remaining in the thermostat at 55° for 115 hours, more of the same restricted diastase (1.305 grams) was added, and a further addition of 1.572 grams was made at the end of 238 hours.

Time.	Diastase added.	$[\alpha]_{D, 55^\circ}$	$R_{55^\circ}$
—	1.432 grams	—	—
65 hours	—   ,,	167.5°	39.2
89   ,,	—   ,,	162.5	38.8
115   ,,	1.305   ,,	—	—
161   ,,	—   ,,	141.8	56.5
238   ,,	1.572   ,,	—	—
281   ,,	—   ,,	137.5	70.5

The quantity of diastase used, which in the final solution corresponds with about 500 grams of malt, renders the constants (especially the specific rotatory powers) untrustworthy, although blank experiments and corrections were made for each addition of diastase.

No insoluble osazone was obtained from the final solution and only a small yield of soluble osazone. When the portion of this solution soluble in 90 per cent. alcohol was evaporated, even in alcoholic solution, it rapidly became brown. This phenomenon, which has been frequently observed by other workers in the case of the products of the hydrolysis of starch by restricted diastase, will be further dis-

cussed in a subsequent paper. The alcoholic solution of the final products of the conversion just described gave no evidence of the presence of maltose, and did not yield crystals even after a considerable lapse of time.

### Series III.

Attempts were now made to follow the reaction with lower temperatures of restriction.

A. Diastase (0.2 gram) was restricted for an hour at 63°, and the solution added to the paste prepared from 10 grams of starch. The solution, which contained rather more than 2 grams in 100 c.c., was placed in the thermostat at 52°.

Time.	$[\alpha]_{D, 52^\circ}$	$R_{3.93}$
43 hours.	150.3°	77.8
91   ,,	148.5	78.3
187   ,,	145.5	82.0

The final solution yielded a small amount of glucosazone when heated with phenylhydrazine acetate. As 0.2 gram of this diastase, if unrestricted, is more than sufficient to convert 10 grams of starch into maltose in 50 hours, it will be seen that apart from the production of glucose the heating at 63° has produced a great alteration. Subsequent experiments showed that by employing a larger amount of the restricted diastase it is possible to carry the reaction still further than the point attained in this experiment at the end of 187 hours.

B. Diastase (0.2 gram) was restricted for 1½ hours at 60°, and added to 10 grams of starch made into paste. The solution, which contained rather more than 2 grams of starch in 100 c.c., was placed in the thermostat at 55°.

Time.	$[\alpha]_{D, 55^\circ}$	$R_{3.93}$
65 hours	144.5°	88.7
113   ,,	145.5	87.9

The final solution was fractionated with alcohol, the portion soluble in 90 per cent. alcohol yielding, on treatment with phenylhydrazine acetate, an osazone (m. p. 150°), entirely soluble in boiling water and consisting of a mixture of the flat plates characteristic of maltosazone with the aggregates of "isomaltosazone."

If the evidence thus far adduced be taken in conjunction with the results published in our earlier paper (*loc. cit.*), it will be seen that when a solution of diastase is heated from 60° to 78°, the enzyme, besides being weakened, is modified, and, in virtue of this modification,

different products result from its action on starch paste. The nature of these products remains to be determined, but we have established the fact that *d*-glucose is formed when the heating of the diastase solution is carried out between 63° and 70°. Later experiments show that *d*-glucose is produced when the heating takes place at higher temperatures (for example, 78°, p. 29) if this is only maintained for a short time.

Having thus established the fact that this modification in the action of the enzyme is a result of its restriction in aqueous solution, it became interesting to ascertain whether this was due to a permanent alteration of the diastase molecule. The question also arose as to whether the *d*-glucose obtained when restricted diastase acts on starch owes its origin to the action of the modified enzyme on maltose, assuming this to be previously formed. As a result of several experiments, we stated (*ibid.*) that *d*-glucose is not produced by the action of restricted diastase on maltose, but the point is so important that it was again investigated.

#### Series IV.

Diastase (6 grams) was heated at 68° for 1½ hours with 100 c.c. of water, the solution filtered and made up to 250 c.c.

(a) Forty c.c. of the solution were added to 15 grams of starch made into paste with 300 c.c. of water.

(b) One hundred and fifty c.c. of the solution were precipitated with alcohol, the diastase collected, and 0.3 gram of the recovered substance dissolved in water at 52°, the solution being added to 15 grams of starch made into paste with 300 c.c. of water. A blank experiment with some of this reprecipitated diastase was carried out at the same time.

(c) Twenty c.c. of the original restricted diastase solution were added to 170 c.c. of a 4 per cent. solution ( $c_{3.93} = 4$ ) of maltose.

The remainder of the original restricted diastase solution was used for a blank experiment.

(a).			(b).		
Time.	$[\alpha]_{D 5.93}$	$R_{3.93}$	Time.	$[\alpha]_{D 5.93}$	$R_{3.93}$
19 hours	153.7°	71.4	17 hours	164.2°	59.3
43 „	151.8	79.1	41 „	154.1	72.2
67 „	150.0	79.4	113 „	153.0	72.3
139 „	147.6	82.0			

*d*-Glucose was produced in considerable amount in both these experiments. It is therefore proved that the alteration of the diastase by heating with water (in this case at 68°) is a permanent one, as it

retains the property of producing a certain amount of *d*-glucose from starch after being precipitated by alcohol and redissolved in water. It is conceivable that *d*-glucose may also result from the action of unrestricted diastase on starch paste, but that it is condensed to a polysaccharide by a secondary action of the enzyme. Experiments to test this point are now in progress.\*

*Experiment c.*—Action of restricted diastase on maltose (see p. 22).

Time.	$[\alpha]_{D 3.93}$	$R_{3.93}$	
19 hours	134.2°	99.96	100.12
139 „	134.0	99.12	99.18

There is no indication from these constants that *d*-glucose is formed by the action of restricted diastase on maltose, and this conclusion is confirmed by the fact that no insoluble osazone was obtainable from the solution. The constants (which, as in all other cases, were fully corrected for the effect of the diastase remaining in the boiled solution) differ from those of pure maltose to an extent beyond the limit of experimental error. To what this is due we cannot at present say.

The following experiment illustrates the action of unrestricted diastase on maltose, giving the constants  $[\alpha]_{D 3.93} = 137.8^\circ$ ,  $R_{3.93} = 100$ . About 3 grams were dissolved in water, a solution of diastase (0.1 gram) added, and the whole made up to 100 c.c. This solution was placed in a thermostat for 48 hours at  $55^\circ$ , and, on examination, gave the following values:  $[\alpha]_{D 3.93} = 131.5^\circ$ ,  $R_{3.93} = 99.5$ .

The solution yielded no glucosazone, but the soluble osazone obtained crystallised in stellate groups of needles and melted at  $169$ – $170^\circ$ . The maltose, after the above-described treatment, was completely fermentable by yeast.

It now became of interest to determine the amount of *d*-glucose formed by the action on starch paste of diastase, restricted for different lengths of time at various temperatures. For this purpose, the sugars in a known volume of the solution were converted into their phenylosazones under standard conditions, and the insoluble glucosazone collected and weighed. After about 50 determinations, the total mixed products were examined and identified as *d*-glucosazone. This result, taken in conjunction with the rotatory and reducing powers possessed by certain fractionated products which gave the insoluble osazone in large amount, proves conclusively that the osazone was derived from *d*-glucose, and that this sugar is one of the products of the action of restricted diastase on starch paste.

\* Compare Ling (*British Association Report*, 1903, and *J. Fed. Inst. Brewing*, 1903, 9, 450).

The osazone, as weighed, melted as a rule at  $198^{\circ}$ ; sometimes, however, the melting point was higher. After being twice recrystallised from alcohol, it melted constantly at  $204^{\circ}$ . When it was dissolved in glacial acetic acid, the solution had a lævorotation (compare E. Fischer, *Ber.*, 1890, 23, 2119).

Maquenne (*Compt. rend.*, 1891, 112, 799) and C. J. Lintner (*Zeit. ges. Brauw.*, 1895, 18, 153) have both devised methods for estimating various sugars as osazones. After numerous trials, we found that, for our purpose, exceedingly concordant results could be obtained in the estimation of *d*-glucose as osazone by working under the following conditions.

Twenty c.c. of the solution, containing 2—3 grams of starch products per 100 c.c., are mixed with 1 c.c. of phenylhydrazine and 1.5 c.c. of 50 per cent. acetic acid in a boiling tube, and heated for an hour in a bath of boiling water. At the end of this time, the liquid, which has evaporated to a small bulk, is carefully poured on to a tared Gooch crucible, and, after the mother liquor is removed, the crystalline glucosazone is transferred to the crucible and washed with a small quantity of boiling water (about 20—30 c.c.), so that the total filtrate does not exceed 50 c.c. It was found that the maximum amount of pure glucosazone could be obtained by one hour's heating. If the heating is continued for a longer time, decomposition of some of the soluble osazones ensues, and the products of this decomposition contaminate the glucosazone. Under these conditions, 0.1 gram of glucose mixed with various proportions of maltose gives 0.0505 gram of glucosazone. In filtering, care must be taken to allow the mother liquor to pass through the Gooch crucible before adding the washing water, otherwise the soluble osazone is precipitated and clogs the filter.

#### Series V.

These experiments were made in order to ascertain what effect the time of previous heating of the diastase solution has on the amount of *d*-glucose formed. The diastase used was prepared from malt germinated by ourselves in the laboratory (see Ling and Davis, *loc. cit.*, p. 484). Three portions of the diastase, amounting each to 0.3 gram, were restricted at  $64^{\circ}$  for 1 hour, 2 hours, and 4 hours respectively. They were then each added to three 15 gram portions of starch made into paste with 300 c.c. of water, the resulting solutions being placed in a thermostat at  $53^{\circ}$ . The following analytical results were obtained:

Time of restriction.	Time of hydrolysis.	$c_{3.93}$ (corr.).	$[\alpha]_{D 3.93}$	$R_{3.93}$	$G_{3.93}$
1 hour	117 hours	4.291	150.7°	78.9	6.5
2 hours	117 „	4.430	154.2	74.1	7.4
4 „	115 „	4.159	154.4	73.1	7.3

These results indicate that, when the time of restricting at 66° is more than an hour, there is no substantial increase in the amount of *d*-glucose formed.

### Series VI.

A freshly prepared active sample of diastase from Odessa malt was employed ; 0.3 gram was used in each experiment and 15 grams of starch. The temperature of restriction was 65—66°.

	Time of hydrolysis in hours.	Time of restriction in hours.			
		0.5.	1.	2.	4.
$c_{3.93}$ (corr.).	17	4.072	4.147	3.873	3.988
	41	4.345	4.384	4.034	4.079
	113	4.088	4.278	3.880	3.965
	209	4.081	4.175	3.829	3.878
$[\alpha]_{D 3.93}$	17	152.6°	154.0°	154.7°	158.4°
	41	144.6	143.5	147.8	153.2
	113	145.3	146.2	147.3	153.3
	209	145.3	147.8	148.8	153.1
$R_{3.93}$	17	74.4	72.6	71.9	66.3
	41	85.4	83.4	81.6	73.4
	113	87.6	85.1	—	73.4
	209	87.1	83.5	81.3	74.5
$G_{3.93}$	17	4.2	4.0	5.1	nil
	41	8.1	8.0	6.3	2.2
	113	9.9	9.2	7.5	8.0
	209	4.3	7.5	3.8	7.5

\* In this experiment, a distinct amount of matter insoluble in boiling water was obtained, but it was amorphous, and therefore not glucosazone.

It is seen by these experiments that for a restriction temperature of 66° the maximum amount of *d*-glucose is formed when the period of

heating was half an hour. It is interesting to note the marked diminution in the percentage of *d*-glucose, after the hydrolysis has proceeded for 209 hours, as compared with the values in the preceding columns (113 hours). This is possibly due to the condensing action of the enzyme.

*Series VII.*

The same diastase was used as in the last series, but the temperature of restriction was 69°. The temperature of hydrolysis was 55°.

	Time of hydrolysis in hours.	Time of restriction in hours.			
		0.25.	0.5.	1.	2.
$c_{3.9}$ (corr.)	17 41 65 137	3.924 3.811 3.724 3.642	4.044 3.876 3.923 3.810	4.092 3.950 — 3.894	3.980 3.919 3.852 3.882
$[\alpha]_{D3.93}$	17 41 65 137	154.6° 141.4 139.1 139.4	157.1° 144.3 143.1 143.0	161.5° 150.8 — 148.5	165.2° 157.7 150.7 151.2
$R_{3.93}$	17 41 65 137	— 91.1 96.6 96.6	— 87.0 89.3 90.8	— 78.4 — 81.4	— 69.4 73.3 75.2
$G_{3.43}$	17 41 65 137	7.8 11.6 11.8 10.8	8.7 11.2 10.6 10.6	5.4 8.2 7.2* 7.9	1.1 7.5 6.5 1.5

\* The exact concentration ( $c_{3.93}$ ) of this solution was not determined, and the figure  $G_{3.93}=7.2$  is calculated on the concentration found for the solution after 41 hours.

*Series VIII.*

In these experiments, the temperature of restriction was raised to 70.5°, but the time of heating was reduced. Temperature of hydrolysis = 55°.

	Time of hydrolysis in hours.	Time of restriction in minutes.			
		5.	17.	30.	120.
$c_{3.93}$ (corr.)	19 43 67	4.079 4.016 3.995	4.121 4.063 4.061	3.985 4.005 3.926	4.027 4.009 3.969
$[\alpha]_{D 3.93}$	19 43 67	151.5° 145.3 144.6	155.4° 147.7 147.3	156.6° 150.9 151.1	166.6° 162.3 162.2
$R_{3.93}$	19 43 67	76.0 86.9 87.8	71.4 82.1 83.9	69.8 78.0 78.6	54.5 61.6 62.1
$G_{3.93}$	19 43 67	6.9 10.4 10.8	8.1 6.8 10.0	5.8 7.9 7.3	4.7 3.7 3.9

## Series IX.

A. 0.3 gram of diastase restricted at 61.5° for 45 minutes and added at 55° to 20 grams of starch made into paste with 400 c.c. of water.

Time of hydrolysis in hours.	$c_{3.93}$ (corr.)			$[\alpha]_{D 3.93}$			$R_{3.93}$		$G_{3.93}$		
	18	42	66	18	42	66	18	66	18	42	66
	4.338	4.255	4.271	148.2°	138.7°	137.8°	81.2	96.2	7.7	3.2	8.0

B. The amounts of diastase shown in the following table were added to 20 grams of starch made into paste with 400 c.c. of water. The temperature of restriction was 70°.

	Time of hydrolysis in hours.	Amount of diastase in grams.		
		0.5.	1.	1.
		Time of restriction in minutes.		
		5.	5.	15.
$c_{3.93}$ (corr.) {	18	4.271	4.107	4.041
	42	4.219	4.082	4.009
	66	4.120	4.077	4.000
$[\alpha]_{D, 3.93}$ {	18	145.6°	141.8°	145.3°
	42	136.1	133.4	135.6
	66	135.3	133.1	135.5
$R_{3.93}$ {	18	84.6	90.1	87.4
	42	98.7	102.4	101.9
	66	99.8	101.6	100.2
$G_{3.93}$ {	18	7.7	—	9.7
	42	9.6	11.4	11.0
	66	10.7	8.9	9.4

C. One gram of diastase was dissolved in water, and the solution, which was raised to a temperature of 73° in 5 minutes and maintained at 73—73.5° for an additional 5 minutes, was then added to 20 grams of starch made into paste with 400 c.c. of water.

Time of hydrolysis in hours.	$c_{3.93}$ (corr.)			$[\alpha]_{D, 3.93}$			$R_{3.93}$		$G_{3.93}$		
	18	42	66	18	42	66	18	66	18	42	66
	3.938	4.990	3.981	153.6°	145.5°	144.7°	77.6	90.0	8.2	8.7	7.6

### Series X.

In this series, solutions containing the weights of diastase given in the table were restricted at the temperatures mentioned, rapidly cooled, and added to paste prepared from 20 grams of starch and 400 c.c. of water at 55° in each case. The hydrolysis was allowed to proceed for 66 hours.

Amount of diastase.	Temperature of restriction.	Time of restriction.	G <sub>3-93</sub> .
0.3 gr.	59.5—60°	1 hour.	0.5
0.3 „	62°	0.25 „	0.4
0.3 „	62°	0.75 „	0.5
1.0 „	76.5—77.5°	5 min.	3.9

In the last experiment, water, at a temperature of 78°, was mixed with the dry diastase, the mixture having initially a temperature of 76.5°. The solution was raised to 77.5° in 5 minutes, after which it was rapidly cooled and added to the starch paste.

### *Conclusions.*

The effect of heating a solution of diastase is to cause a weakening of the action of the enzyme, and also to produce an alteration in the diastase molecule. The latter effect, which is the more important in the foregoing experiments, is a permanent one, for diastase solution which has been heated above 55° retains its altered properties when reprecipitated from a solution by alcohol and allowed to act on starch paste at a temperature of 55° or below.

The alteration of the diastase appears to commence when a solution is heated below 60°, although a complete change is not effected, inasmuch as the amount of *d*-glucose formed by the action on starch paste of diastase, previously heated for an hour at this temperature, is small.

As the temperature of restriction is increased, the amount of *d*-glucose formed by the action of the enzyme on starch is augmented, and the maximum amount of *d*-glucose is produced by diastase which has been previously heated in solution at 68—70°. Above this temperature, the weakening of the enzyme is so rapid that a much larger quantity of it has to be employed in order to attain the stage of the reaction at which *d*-glucose appears, especially if the heating is prolonged; nevertheless, this hexose is formed by diastase restricted at temperatures up to 78°, and probably above this.

It has invariably been observed that, when the solution is kept at the temperature of hydrolysis, usually 55°, after the maximum amount of *d*-glucose has been formed, this sugar diminishes in amount, and the occurrence of this apparently condensing action of the enzyme may probably explain the occasional failure to detect *d*-glucose among the products of hydrolysis (see Series I and II). In any case, the maximum amount of *d*-glucose formed does not exceed 12 per cent. of the total hydrolytic products.

## V.—*The Action of Halogens on Compounds containing the Carbonyl Group.*

By ARTHUR LAPWORTH.

THE question of the nature of the mechanism of substitution in carbon compounds has attracted much attention during recent years, more especially in certain cases where the compounds are benzenoid in character and in which the process of substitution in the aromatic nucleus appears to involve the initial formation of an additive product of the compounds with the agent used or of an intermediate substitution product in which the substituting atom or group is not found in its final position of attachment.

Considerably less is known of the mode in which substitution occurs in fatty compounds; and in what is possibly the simplest case of all, namely, that of direct substitution such as occurs among the paraffins, it may be said that there is no evidence which affords any real assistance in arriving at conclusions as to the mechanism of the process, and generally these cases have been avoided as being the most difficult to solve.

The case of substitution in the group of compounds containing the complex  $\text{:CH}\cdot\text{CO}$ , such as ketones, aldehydes, carboxylic acids and their derivatives, is one of considerable interest, and in certain aspects has aroused much discussion, for there is here a possibility that the characteristic replaceability of the  $\alpha$ -hydrogen atom may be not a direct process, but one due to the initial formation of the enolic form  $\text{:C:C(OH)}\cdot$ , and this view has appeared more probable since it has been shown that the nitro-paraffins, which in many respects resemble carbonyl compounds, are apparently not capable of being brominated directly, but are easily converted into monobromo-derivatives if they are first transformed into the isonitro-form which corresponds with the enolic forms of carbonyl compounds. It is a general rule, too, that those carbonyl compounds are the most easily attacked which are known to be capable of conversion into their enolic forms or one of the corresponding metallic derivatives.

The difficulty with which the paraffins are attacked by halogens renders this question of the mechanism of their substitution most difficult to investigate in a satisfactory way, and it seems desirable, therefore, that search should be made for some other class of more easily substituted compounds in which the process is direct, at least in the same sense as it probably is in the paraffin series, and the work described in the present paper was commenced in the hope that, after all, the bromination of simple ketones might prove to be mainly the

result of "direct" substitution. The results obtained, however, can only be interpreted on the opposite assumption; briefly stated, they were as follows.

The action of bromine on acetone in dilute aqueous solution is exceedingly slow, but becomes more rapid in presence of acids, the resulting accelerations being of the same order in the case of the more powerful mineral acids (sulphuric, hydrochloric, and nitric acids), and less obvious in the case of the weaker ones, such as acetic acid. The influence of hydrochloric acid on the velocity was not appreciably affected by the presence of an equivalent amount of potassium chloride or bromide. Neutral salts of strong bases and acids in general did not produce any marked influence on the speed of reaction. It was noticed, too, that the velocity observed in diffused daylight was not appreciably different from that in darkness.

The effect of the three mineral acids was nearly proportional to the amounts used, but in the case of sulphuric acid, between the concentrations 0.04- and 0.40-normal, the effect was proportionately slightly greater as the dilution increased. The velocity was nearly proportional to the concentration of acetone, but was practically independent of the concentration of the bromine.

Discussing these points in the reverse order, it may be observed that the independence of the velocity of reaction on the concentration of bromine shows clearly, first, that the reaction proceeds in at least two stages, in one or more of which the bromine is not involved, and, secondly, that in the stage or stages in which the bromine takes part, the velocity of reaction is so great that the time occupied is not measurable.

The approximate proportionality of the velocity to the concentration of the acetone indicates that in the reaction representing that stage, the velocity of which is measured, only one molecule of acetone takes part, whilst the observations as to the influence of acids of different concentration are best explained on the supposition that in this reaction one hydrogen ion is involved.

The increasing degree of dissociation of sulphuric acid due to dilution becomes apparent in the slight increase of the velocity constants representing the speed of absorption of bromine per equivalent of acid per litre.

The effects produced by sulphuric, nitric, and hydrochloric acids at the concentrations 0.40-normal were represented approximately by the numbers 1.19, 1.20, 1.36. These numbers, although of the same order of magnitude, are not proportional to the respective concentrations of the hydrogen ions. This discrepancy, however, is not without parallel, and does not militate seriously against the foregoing general conclusion.

It seems probable, then, that the bromination of acetone under the

conditions maintained is best regarded as the result of a slow, reversible change effected in the acetone by the hydrogen ions, followed by an almost instantaneous bromination of the product, a change which is not appreciably reversible. This intermediate product is perhaps the enolic form of the ketone, as it has been already shown that in many cases the rapid attainment of equilibrium between the tautomeric forms of carbonyl compounds is brought about by acids (Trans., 1902, 81, 1503, and 1903, 83, 1121), whilst there is ample reason for believing that the enolic forms are the more rapidly attacked by substituting agents.

It is clear, also, that the independence of the speed of reaction on the concentration of bromine shows that the velocity with which the second form of the acetone is brominated must be incomparably greater than that of the reverse change of the labile to the normal form, so that the observed velocity is a fairly precise measure of the speed with which acetone is converted from the normal into the less stable form.

In the case of the interaction of chlorine and acetone, the speed of reaction is more obviously dependent on the concentration of the halogen, but as that concentration diminishes, the velocity decreases until it approximates very nearly to that observed when bromine is used under similar conditions. This difference might be explained in at least two ways: (1) that chlorine acts directly on acetone, or (2) that the halogen is capable of existing in the initial change in the ketone which precedes the actual substitution. Of these, however, the first possibility is apparently disposed of by experiments on the action of chlorine on neutral solutions of acetone, as in this case the initial velocity of reaction is far too small to account for the difference in the speeds with which chlorine and bromine are absorbed by acetone in presence of acid: in both cases, the speed increases with lapse of time, owing, doubtless, to the increasing amount of acid present.

The last part of the paper contains an account of some experiments which were made for the purpose of ascertaining whether the action of chlorine and bromine on other carbonyl compounds is accelerated by acids, and the results show beyond question that the effect is a fairly general one and is well marked in the case of acetone and other ketones in solvents other than water, and also in those of carboxylic acids and their anhydrides and esters.

The ease with which dry acetic acid may be brominated in presence of halogen hydrides leads to a simple explanation of the part played by small quantities of phosphorus in promoting the action of halogens on carboxylic acids. The phosphorus chlorides and bromides which are produced in the first instance, will react so as to remove the water present, supplying at the same time the requisite hydrogen chloride or bromine; in the absence of water, the halogen hydrides

will be produced by the interaction of the phosphorus halogen compounds with some of the carboxylic acid itself. The usual explanation, namely, that the halogen only attacks the acid chloride or bromide is no longer necessary since it has been shown that the accelerating effect of powerful acids is not confined to substitutive changes in the series of carboxylic acids.

### EXPERIMENTAL.

#### *Bromination of Acetone.*

The action of bromine on acetone, either undiluted or dissolved in organic solvents, is difficult to control, and dilute aqueous solutions of the ketone were therefore employed, the experiments being made with the object of ascertaining, first, the effect of varying concentrations of acetone and bromine, and, secondly, the effects produced by foreign substances which might reasonably be expected to alter the velocity of reaction, either by their influence on the state of dissociation of the reacting substances or by retarding or accelerating the changes of structure which the ketone might undergo.

In the preliminary experiments, a dilute aqueous solution of acetone was rendered yellow by the addition of bromine water and then divided between a number of stoppered bottles, to each of which was then added varying quantities of a number of electrolytes. The results showed clearly that the effect of neutral salts, such as sodium sulphate, potassium bromide, &c., was very slight, but that acids caused a very marked increase in the speed with which the colour of the bromine disappeared, so that, instead of occupying some days or even weeks, the action was at an end in a few hours or minutes, according to the affinity and the amount of acid present. Thus with equivalent amounts of sulphuric acid, hydrochloric acid, and acetic acid, the first two acted very rapidly, and the last caused a marked acceleration; with acetic acid in presence of an excess of sodium acetate,\* the change was almost as slow as in the absence of acids.

In order to ascertain whether the product of the action of bromine on acetone in presence of dilute mineral acid was a simple substitution product, 30 grams of acetone were dissolved in a mixture of 200 c.c. of water and 50 c.c. of ordinary hydrochloric acid, the whole being allowed to remain for several weeks in a stoppered vessel with one molecular proportion of bromine. After the colour of the solution had entirely disappeared, the solution was filtered from a very small

\* In this instance it was found necessary to submit the sodium acetate to a preliminary treatment with a small quantity of bromine, the excess of which was afterwards removed by a stream of air, as the salt invariably absorbed a small quantity of halogen even after repeated crystallisation.

quantity of crystalline matter, cooled in ice, and saturated with calcium chloride, the oil which separated being removed, dried, and fractionally distilled.

The crystalline material was insoluble in water and crystallised from ethyl acetate in fine needles melting at  $75^{\circ}$ .

0.3112 gave 0.6483 AgBr. Br = 88.6.

$C_3H_5OBr_5$  requires Br = 88.5 per cent.

The compound appeared to agree in all its properties with the penta-bromoacetone melting at  $76^{\circ}$ .

The liquid portion of the product had the characteristic pungent odour of bromoacetone, and, when rapidly distilled under atmospheric pressure, passed over for the most part between  $130^{\circ}$  and  $142^{\circ}$ , a certain amount of a dark brown residue remaining in the flask. The fraction boiling at  $130$ — $142^{\circ}$  was washed with dilute sodium carbonate solution to remove the hydrogen bromide liberated during the distillation, dried over anhydrous sodium sulphate, and analysed.

0.1685 gave 0.2338 AgBr. Br = 59.0.

$C_3H_5OBr$  requires Br = 58.4 per cent.

There is therefore no reason to suppose that the reaction between acetone and bromine in presence of dilute acids is in any way abnormal. It may be mentioned that in the quantitative experiments described below the products invariably had the pungent odour of bromoacetone.

A series of quantitative experiments was made with a dilute aqueous solution of acetone at a constant temperature, the concentration of the bromine being determined from time to time by withdrawing aliquot portions of the solution by means of a pipette, and running these directly into a solution of potassium iodide; the amount of iodine liberated was ascertained by titration with a 0.05-normal solution of sodium thiosulphate, the exact value of which was checked from time to time.

The concentration of the acetone was kept somewhat low in order that its condition of hydration might be as nearly as possible the same in different experiments, which will only be the case in dilute solution. Moreover, the relative amount of bromine employed at first was always considerably less than one molecular proportion, so that the concentration of the unsubstituted portion of the acetone should not vary too widely; it was found, as a matter of fact, that within the limits adopted the relative initial concentrations of the bromine and acetone did not appreciably affect the nature of the results.

In every case in which a flask had to be opened several times during an operation, so that a measurable quantity of volatile materials might

have escaped, a second flask was prepared simultaneously, in precisely the same way, and opened for titration only at the beginning and at the end of the experiment; in the few cases in which the titres did not correspond, the results were rejected. Further, in order that the results should have at least a comparative value, the correct working of the thermostat and the concentration of the solutions were tested by another determination of the velocity of reaction in a solution of standard concentration, so that any material variation in the conditions could be readily detected and the necessary allowance made. These measurements were, however, made with the object of ascertaining the general character of the influence of the materials employed, and are to be regarded as approximations only, but it is probably safe to suppose them comparable.

The speed of removal of bromine by a dilute aqueous solution of acetone in the absence of free acid or alkali is very small; thus, in a solution containing 40 grams of acetone per litre, the free bromine at the commencement of the experiment corresponded with 9.25 c.c. of  $N/20$  thiosulphate per 25 c.c. of the solution, whilst at the end of three days, during which time it remained at the temperature of the laboratory, the titre had only diminished to 9.05, and at the end of a week it was 8.70.

In the presence of acid, the speed of disappearance of the bromine was nearly constant. The numbers obtained in the following experiments, in which the concentration of acetone and sulphuric acid, as well as the temperature, are those which were adopted throughout as the standard for comparison, prove clearly that the speed at the end of the operation is practically identical with that at the commencement. The temperature throughout the series of experiments was  $20.3^{\circ}$ , except where a statement to the contrary occurs. The titres are those for 25 c.c. of solution, and are given in terms of  $N/20$  thiosulphate; the initial and final numbers are expressed in the same terms, but were always determined by the titration of 50 c.c. of the solution, so that the numbers in these cases are one-half of those actually obtained, and were used throughout for the determination of the approximate value of the constant  $k$ , this term being found by the aid of the formula:

$$k = 10^4 \times V/c_1c_2,$$

where  $V$  is the velocity of disappearance of free bromine in gram-molecules per litre, and  $c_1$  and  $c_2$  are the concentrations of the ketone in gram-molecules, and of the acid in gram-equivalents per litre respectively.

The numbers in the third column of the following table are those calculated on the assumption that the reaction may be represented by a straight line between the initial and final points.

*Experiment A.*

Quantities employed : acetone = 40 grams ; normal  $\text{H}_2\text{SO}_4$  = 400 c.c. per litre.

Time.	Titre.	Calculated.
0	19.25	—
10 minutes	17.05	16.95
20    ,,	14.80	14.60
60    ,,	5.00	5.30
67    ,,	3.50	3.65
70    ,,	3.00	3.05
75    ,,	1.60	1.90
80    ,,	0.65	0.75
83    ,,	0.05	—
$k = 8.38$		

Two other experiments with the same concentrations of acid and ketone gave  $k = 8.52$  and  $8.57$ .

As these experiments indicated that the velocity of bromination was nearly independent of the amount of bromine present, two other experiments were made with small quantities of the halogens and these confirmed this conclusion, the same rectilinear character being evident and the constants found being (*B*)  $8.40$  and (*C*)  $8.55$ .

In Fig. I (p. 37), the results of the last two experiments are compared with those given in the foregoing table.

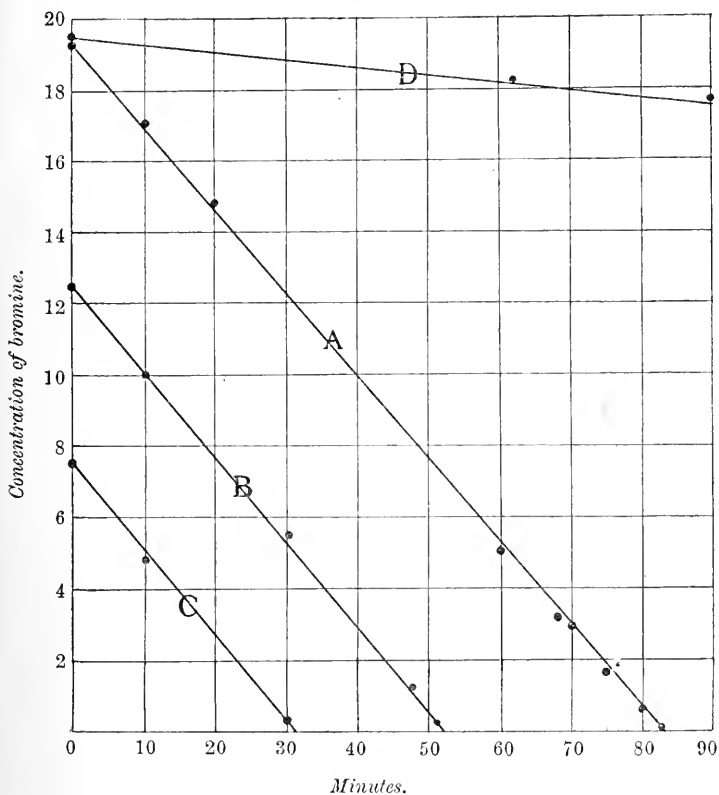
In order to determine whether the initial change produced in the ketone by the acid was a reversible one, a solution containing 40 grams of acetone and 400 c.c. of normal sulphuric acid was prepared and allowed to remain for four days, when a measured bulk of bromine water was added and the whole at once diluted to one litre with water at  $20.3^\circ$ , an exactly similar solution being made simultaneously in which the ketone and acid were brought into contact only at the last moment. It was found that the titres of 25 c.c. of these solutions, five minutes after making up, were 17.2 and 17.4 respectively, whilst the corresponding velocity constants were  $k = 8.31$  and  $8.43$  respectively ; it seems clear, therefore, that the initial change occurs only to a very minute extent and is of a reversible character.

*Effect of the Concentration of Ketone and Acid.*—The line *D* in Fig. I represents a portion of a line joining the points corresponding with the initial and final titres obtained in an experiment in which the concentration of the acetone is only one-tenth of that present in *A*, *B*, and *C* ; the reaction velocity was somewhat less than a tenth of that observed in the other three cases.

The mean results obtained in a number of experiments at  $20.3^{\circ}$  are given in the following table, and represent the variation of  $k = 10^4 \times V/c_1c_2$  with the concentration of ketone and acid.

Sulphuric acid.	Acetone (grams per litre)			
	4	10	20	40
0.40 gram-mols. per litre	8.07	8.24	8.38	8.49
0.20                    "	—	8.53	8.59	8.71
0.10                    "	—	—	8.81	8.93
0.04                    "	—	—	—	9.68

FIG. 1.



With hydrochloric and nitric acids at a concentration of 0.40 gram-molecules per litre and 40 grams of acetone per litre, the reaction was also rectilinear, the constants found being 11.56 and 10.21 respectively. In presence of potassium chloride and bromide with hydrochloric acid of the above concentration, the constants ( $k$ ) were 11.69 and 11.54 respectively, in both cases, an amount of

the salt equivalent to the acid present being employed. The results obtained with 0.40-normal acetic acid were very inconsistent, a rapid fall in the bromine concentration being observed at first and due perhaps to some impurity in the acetic acid, which was not readily removed, even by distillation over sodium acetate. With acetic acid in the presence of two equivalents of sodium acetate which had been purified by a preliminary treatment with bromine, a rapid initial fall in the titre from 16.80 to 14.25 occurred in the course of a quarter of an hour, whilst subsequently the action became so slow that after an additional period of five days the titre had fallen only to 13.90.

*Chlorine and Acetone.*

On the whole, it was found that when chlorine was allowed to act on acetone in dilute aqueous solution in presence of mineral acids, this halogen invariably disappeared somewhat more rapidly than bromine. The following details of two simultaneous series of measurements made with two solutions of identical concentration as to acetone and acid will serve to show what was the general nature of the difference observed in the two cases.

Quantities employed: acetone = 20 grams per litre; normal  $\text{H}_2\text{SO}_4$  = 400 c.c. per litre.

A. Bromine.		B. Chlorine.	
Time.	Titre.	Time.	Titre.
0	9.20 c.c.	0	(?)
12.5 minutes	7.75 "	11.0 minutes	11.00 c.c.
34.0 "	5.45 "	19.0 "	8.90 "
65.5 "	1.80 "	26.0 "	7.70 "
71.5 "	1.15 "	38.5 "	5.65 "
77.5 "	0.40 "	47.0 "	4.50 "
		55.5 "	3.40 "
		64.0 "	2.25 "
		74.0 "	1.10 "
		81.0 "	0.35 "

It will be noticed that the chlorine at first disappears with considerably the greater speed, but, as the concentration of the halogen diminishes, the velocity of chlorination approaches very nearly to that of bromination, so that it appears that the velocity of substitution is not so nearly independent of the concentration of the halogen in the former as in the latter case.

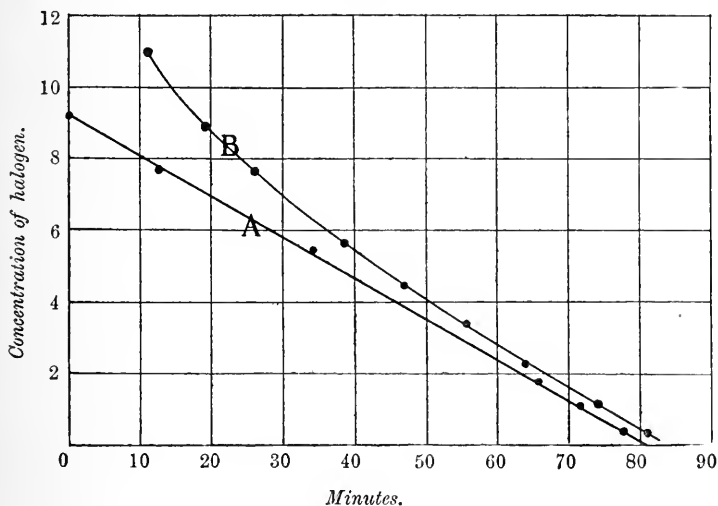
To test the question as to whether chlorine exerts an independent or direct influence on the speed of substitution, the effects of the two halogens on dilute, initially neutral, aqueous solutions of acetone were

directly compared and the following results obtained, the concentration of the acetone being 40 grams per litre.

A. Bromine.			B. Chlorine.		
Time.	Titre.		Time.	Titre.	
0	10.70	c.c.	0	9.95	c.c.
4 hrs. 5'	10.45	"	3 hrs. 6'	9.85	"
23 " 53'	10.70	"	23 " 6'	9.55	"
87 " 3'	10.30	"	87 " 0'	7.60	"
168 " 0'	9.10	"	168 " 0'	2.40	"

Thus the action of chlorine alone on acetone is very slow indeed and does not account for the very considerable difference between the initial velocities of chlorination and bromination in the presence of acid.

FIG. 2.



#### *Bromination of Acetone in Solvents other than Water.*

Specimens of purified light petroleum, benzene, and chloroform were allowed to remain in contact with bromine for some hours and were then washed repeatedly with dilute alkali and water and finally dried. This treatment was found to be necessary, as almost all specimens of these liquids were found to decolorise a small quantity of bromine, and the subsequent action of bromine on acetone dissolved in them was much too rapid for comparative experiments, owing, probably, to the production of free hydrogen bromide.

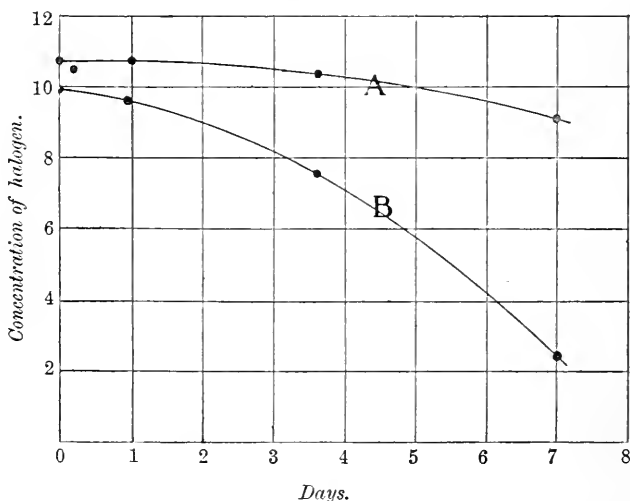
Highly dilute solutions of acetone, hydrogen chloride, and bromine

in the purified solvents were then prepared, and it was found on mixing the solutions of acetone and bromine that the disappearance of the colour of the latter was conveniently slow at first and that addition of the hydrogen chloride solution produced a very marked acceleration. It was also observed that, when no hydrogen chloride was added, the disappearance of successive small quantities of bromine occurred with increasing rapidity, owing, no doubt, to the hydrogen bromide formed.

*Effect of Acids on the Speed of Bromination and Chlorination of other Carbonyl Compounds.*

Many ketones are not, at first, easily attacked by bromine, but when once the reaction has begun it proceeds rapidly. This effect

FIG. 3.



may be noticed when, for example, methyl isopropyl ketone is treated with bromine in the cold or when  $\alpha$ -bromocamphor is prepared by adding bromine to camphor which is being heated on the water-bath.

Acetic anhydride, when mixed with bromine at the ordinary temperature, is only very slowly affected, but, if previously saturated with hydrogen chloride or if mixed with a few drops of sulphuric acid and subsequently cooled, is so readily attacked that on the addition of bromine the temperature rises appreciably and in the course of a few minutes the colour of the halogen may disappear.

Diethyl malonate was examined as a type of ester which is comparatively easily brominated. When this substance is mixed with purified bromine at the ordinary temperature, no marked effect is noticeable, often during the course of some hours; in presence of a small quantity of hydrogen chloride, however, the action proceeds very rapidly, even if the temperature is kept low. A striking experiment may be made by mixing a few grams of the ester with an approximately equal bulk of bromine in the cold; a few drops of the mixture are warmed in a test-tube over a Bunsen burner, and when the resulting action is complete the fuming product is cooled and added to the bulk of the mixture; a violent reaction soon occurs, hydrogen bromide is evolved in large quantities, and the colour of the liquid changes from a deep brown to a very pale yellow, the change being usually complete in less than a minute.

Acetic acid was chosen to illustrate the case of acids. As is well known, bromine scarcely acts on acetic acid even at its boiling point, and it was found that, even when saturated with hydrogen chloride or bromide, this acid, when containing 1 or 2 per cent. of water, is only slowly attacked by the halogen at the temperature of the water-bath. If, however, it is repeatedly purified by freezing, it becomes easy to prepare bromoacetic acid, first by saturating the dry product with hydrogen chloride, and then by warming it at 80—90° with a slight excess of bromine: thus, from 33 grams of 99 per cent. acetic acid saturated with hydrogen chloride, a yield of 54 grams of bromoacetic acid or 71 per cent. of the calculated amount was obtained after 9 hours' heating with bromine on the water-bath.

In another experiment, 100 grams of the acid containing 95 per cent. of pure acetic acid were mixed with 22 grams of acetyl chloride for the purpose of removing water and affording simultaneously the requisite hydrogen chloride. After 42 grams of this mixture had been heated for 5 hours on the water-bath, the product was treated with successive quantities of bromine and distilled at the end of 6 hours; a yield of 83 grams of crystalline bromoacetic acid was thus obtained corresponding with about 85 per cent. of the calculated amount.

The effect of chlorine on dry acetic acid is similar; in diffused daylight, acetic acid saturated with hydrogen chloride was only slowly chlorinated at 100°, but this is also the case when phosphorus is employed, and the speed in the two cases appears to be very similar. It is probable, therefore, that in direct sunlight the yield by this process might be as good and the action as rapid as in the ordinary method, but no opportunity was obtained of trying the reaction under these conditions.

The author is indebted to the Research Fund Committee of the Chemical Society for a Grant which defrayed some of the cost of the investigation.

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## VI.—*Derivatives of Menthyl Cyanoacetate.*

By DOUGLAS ANDERSON BOWACK and ARTHUR LAPWORTH.

THE esters of acetoacetic, cyanoacetic, and malonic acids contain hydrogen atoms, which, although directly attached to carbon atoms, are easily replaced by sodium, and the resulting metallic derivatives, at least in the case of the first two classes, appear to be derived from the enolic modifications of the esters. The stability of the enolic forms of the free esters appears to vary considerably, and only in the case of the derivatives of the acetoacetates is there any direct evidence that a measurable amount of free enol is present when an equilibrium is attained. In the hope of obtaining further evidence on this point, some optically active derivatives of cyanoacetic acid were prepared, with the view of determining whether they exhibited any measurable mutarotation, as this phenomenon is apparently always associated with change in molecular structure, and, moreover, was well marked in the case of certain derivatives of menthyl acetoacetate (Trans., 1902, 81, 1502, and 1903, 83, 1117).

The following investigation had been practically completed when a paper by Tschugaeff appeared (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 6069), in which the rotatory power of menthyl cyanoacetate was given, so that the first compound described in the present paper is not new.

We have not been able to consult the original paper, but the rotatory power of the ester as given in an abstract (Abstr., 1903, ii, 1) agrees satisfactorily with the number we had previously obtained.

Menthyl cyanoacetate does not appear to exhibit a trace of mutarotation, even in presence of traces of bases or acids, agents which have been found to accelerate this change whenever it occurs. The rotatory power of the monobromo-derivative in benzene, however, altered somewhat rapidly from  $[\alpha]_D - 23.42^\circ$  to  $[\alpha]_D - 32.97^\circ$ .

It was expected that if mutarotation occurred in any of the derivatives of this ester, it would probably be most readily detected in the azo-compounds, particularly as the azo-derivatives of menthyl aceto-

acetate exhibited this property in an extraordinary degree (compare Trans., 1903, 83, 1117). Moreover, Weissbach (*J. pr. Chem.*, 1903, [ii], 67, 395) has shown that ethyl phenylazocycanoacetate may be obtained in three different forms, two of which he regards as stereoisomeric azocycanoacetates, and the third as ethyl  $\alpha$ -phenylhydrazonocycanoacetate. No appreciable change in the rotatory powers of the menthyl esters, however, could be detected.

It is worthy of note that the rotatory powers of the azo-compounds described in the present paper, unlike those of menthyl acetoacetate (compare Trans., 1903, 83, 1117), are within the usual limits found for menthyl esters of ordinary carboxylic acids. Menthyl bromocycanoacetate, however, has initially an abnormally small rotatory power, which, as in similar cases, may perhaps be due to the presence of the asymmetric carbon atom present in the acyl residue.

#### EXPERIMENTAL.

##### *Menthyl Cyanoacetate*, $\text{CN} \cdot \text{CH}_2 \cdot \text{CO}_2 \cdot \text{C}_{10}\text{H}_{19}$ .

Menthol (43 grams) and ethyl cyanoacetate (30 grams), mixed in a distilling flask connected with a condenser, are gently heated over an Argand burner at such a temperature that about one drop of alcohol per minute is collected, and the heating is continued until the theoretical amount of liquid has thus been obtained. The product is then submitted to fractional distillation under a pressure of about 30 mm., so as to remove the considerable amount of menthene which is always formed; when the temperature of the vapour has risen to about  $150^\circ$ , the distillation is interrupted, and the residue, which partly solidifies on cooling, is triturated with alcohol and spread on porous earthenware, the solid being finally recrystallised from alcohol.

0.2018 gave 0.5167  $\text{CO}_2$  and 0.1726  $\text{H}_2\text{O}$ .  $\text{C} = 69.8$ ;  $\text{H} = 9.5$ .

$\text{C}_{13}\text{H}_{21}\text{O}_2\text{N}$  requires  $\text{C} = 70.0$ ;  $\text{H} = 9.4$  per cent.

The ester is somewhat readily soluble in most of the ordinary organic media, and crystallises from alcohol in well-defined, small prisms or flat needles melting at  $83-84^\circ$ .

In plane polarised light, the crystals show straight extinction, and the directions of greatest elasticity and length are coincident, the double refraction being strong.

When melted between glass slips, the compound solidifies readily in very long, flat needles, crystallographically identical with those obtained from alcohol; in these, the optic axial plane cuts the crystals longitudinally, and in some cases a bisectrix, probably the obtuse, of a figure of wide angle, emerges normally to the field, so that the acute

bisectrix is probably emergent at the apices of the crystals. For the determination of the rotatory power, a solution of 0.5000 gram of the ester in benzene (25 c.c.) was examined in a 2 dm. tube; the rotation observed was  $\alpha_D = -3.25^\circ$ , giving  $[\alpha]_D = -81.15^\circ$ ; no alteration of this value was noticed after the lapse of some days, and no change was effected by the introduction of traces of piperidine or trichloroacetic acid. The rotatory power of menthyl cyanoacetate was given by Tschugaeff as  $[\alpha]_D = -80.71^\circ$  (*loc. cit.*).

*Menthyl bromocyanoacetate*,  $\text{CN}\cdot\text{CHBr}\cdot\text{CO}_2\cdot\text{C}_{10}\text{H}_{19}$ , was made by adding the requisite quantity of bromine to a solution of menthyl cyanoacetate in chloroform, the product being allowed to remain until the reaction was complete, when it was shaken repeatedly with water, dried over calcium chloride and evaporated, the solid residue being then crystallised from alcohol.

0.1908 gave 0.1176 AgBr.  $\text{Br} = 26.4$ .

$\text{C}_{13}\text{H}_{20}\text{O}_2\text{NBr}$  requires  $\text{Br} = 26.5$  per cent.

The substance is somewhat readily soluble in chloroform, benzene, and glacial acetic acid, but more sparingly so in alcohol and light petroleum. It separates from alcohol in well-defined, small prisms, which in plane polarised light have straight extinction and strong double refraction, the directions of greatest length and elasticity being coincident; when melted between glass slips, it solidifies in masses of very small, ill-defined, flat needles.

For the determination of the optical activity, a solution of 0.4056 gram of the compound dissolved in benzene (25 c.c.) had an initial rotation in a 2 dm. tube of  $\alpha_D = 0.76^\circ$ , whence  $[\alpha]_D = -23.42^\circ$ . The value rose within half an hour to  $[\alpha]_D = -32.9^\circ$ , afterwards remaining constant at this point.

*Menthyl p-Tolylazocyanoacetate*,  $\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\cdot\text{C}_{10}\text{H}_{19}$ .

It was not found possible to obtain menthyl phenylazoacetate in a crystalline form, but the preparation of the corresponding *p*-tolylazo-compound presented little difficulty. Menthyl cyanoacetate was dissolved in a large quantity of warm alcohol containing an excess of sodium acetate, and to the well-cooled liquid was slowly added one molecular proportion of *p*-tolyl diazonium sulphate dissolved in the smallest possible quantity of water. After some hours, during which the mixture remained at the temperature of the laboratory, the whole was poured into water and the deposited oil collected, washed repeatedly with water, and dissolved in an equal bulk of alcohol. After some weeks, the azo-compound was deposited in large crystals, which were freed from adherent oil and recrystallised from alcohol.

0.2120 gave 0.5467  $\text{CO}_2$  and 0.1509  $\text{H}_2\text{O}$ .  $\text{C} = 70.3$ ;  $\text{H} = 7.9$ .

$\text{C}_{20}\text{H}_{27}\text{O}_2\text{N}_3$  requires  $\text{C} = 70.4$ ;  $\text{H} = 7.9$  per cent.

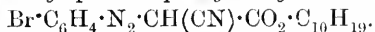
The compound dissolves readily in ether, ethyl acetate, acetic acid, chloroform, and benzene, but is much more sparingly soluble in alcohol and light petroleum. It separates very slowly from warm supersaturated solutions in alcohol in the form of beautiful, large, transparent, yellow plates which melt at  $93-95^\circ$ . When crushed fragments of the crystals are examined in cedar-wood oil in convergent polarised light, a biaxial interference figure of wide angle is occasionally noticeable. If, as is probable, the figures observed were those surrounding the acute bisectrix, the double refraction is positive in sign and strong. After melting between glass slips, the substance could not be made to resolidify.

For the determination of the optical activity, a solution of 0.7543 gram of the compound in benzene (50 c.c.) was examined in a 2 dm. tube. The rotation observed as a mean of several concordant readings was  $\alpha_D = -1.62^\circ$ , whence  $[\alpha]_D = -53.7^\circ$ .

The rotatory power did not change after the solution had remained for several days; the addition of piperidine, however, caused an immediate alteration of the observed rotation by  $0.04^\circ$ , but this new value was also constant, so that the change was probably not due to mutarotation; no effect was produced by the addition of trichloroacetic acid.

The azo-compound does not appear to dissolve in cold 30 per cent. aqueous sodium hydroxide, even if very finely powdered, and it communicates no colour whatever to the liquid; even if the alkali is added to the alcoholic solution of the substance, when the liquid is poured into water, the latter is found to be colourless after the precipitate has settled. The corresponding ethyl ester dissolves somewhat readily in dilute alkali, and the difference in properties between the two esters is doubtless to be attributed to the very great relative difference between their solubilities in water rather than to any chemical dissimilarity (compare Trans., 1903, 83, 1117).

*Menthyl p-Bromophenylazocynoacetate,*



This compound was prepared by a method exactly similar to that used in making the foregoing compound. It crystallised readily when its alcoholic solution was sown with a trace of the crystals of the corresponding *p*-tolyl compound.

0.2005 gave 0.4155  $\text{CO}_2$  and 0.1092  $\text{H}_2\text{O}$ .  $\text{C} = 56.5$ ;  $\text{H} = 6.0$ .

$\text{C}_{19}\text{H}_{24}\text{O}_2\text{N}_3\text{Br}$  requires  $\text{C} = 56.15$ ;  $\text{H} = 5.9$  per cent.

The substance closely resembles that just described in regard to its solubility in various media, but appears to be somewhat less readily soluble. It separates from warm alcohol in the form of magnificent, transparent, yellow prisms or thick plates which melt at 97—98°. Crystallographically, the description given of the *p*-tolyl compound applies equally well to the present substance. Occasionally it was found that another form of the compound separated during the crystallisation from alcohol. This modification presented the appearance of very fine needles and melted somewhat indefinitely between 95° and 105°. The difference between the two forms, however, appears to be of a crystallographical and not a chemical character, as the rotatory powers in both cases are constant and identical, and by seeding the supersaturated solution of the acicular modification with a trace of the other the whole may be converted into the transparent tables characteristic of the form melting at 97—98°.

For the determination of the rotatory power, a solution containing 0.3450 gram dissolved in benzene (25 c.c.) was examined in a 2 dm. tube. The rotation observed was  $\alpha_D = -1.18^\circ$ , whence  $[\alpha]_D = -42.75^\circ$ .

The authors desire to express their thanks to the Research Fund Committee of the Chemical Society for a grant which defrayed part of the cost of the investigation.

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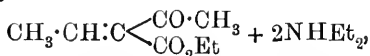
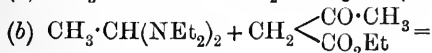
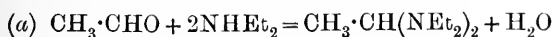
## VII.—*Optically Active Esters of $\beta$ -Ketonic and $\beta$ -Aldehydic Acids. Part IV. Condensation of Aldehydes with Menthyl Acetoacetate.*

By ARCHIE CECIL OSBORN HANN and ARTHUR LAPWORTH.

THE only  $\alpha$ -substituted derivatives of menthyl acetoacetate which have yet been described are the azo-compounds (Trans., 1903, 83, 1114), which have been isolated in a solid condition and found to exhibit mutarotation in a very marked degree. All attempts to prepare the ordinary  $\alpha$ -alkyl substituted derivatives, on the other hand, have failed, probably because, as obtained by the ordinary methods, they are mixtures of fusible isomerides, that is to say, of the *l*-menthyl esters of the *d*- and *l*-alkylacetoacetates.

Many of the alkylidenediaceoacetates, however, may be isolated

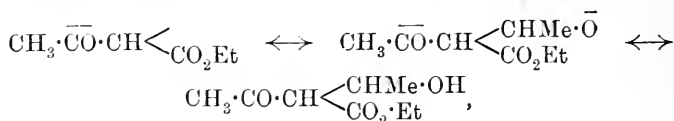
without difficulty in crystalline and apparently homogeneous forms. The method used in preparing them was usually that employed by Knoevenagel (*Annalen*, 1894, 281, 25; *Ber.*, 1894, 27, 2345, &c.), namely, by treating a mixture of the alkyl acetoacetate and an aldehyde with an organic base as a condensing agent. This synthesis has been shown by its discoverer to proceed in two stages, in the first of which condensation takes place between one molecule of the aldehyde and one of the ester, yielding the unsaturated alkylidenemonoacetoacetate,  $\text{CR}:\text{C}(\text{CO}_2\text{Alk})\cdot\text{CO}\cdot\text{CH}_3$ , whilst in the second stage the above product unites with another molecule of the original alkyl acetoacetate affording the alkylidenebisacetoacetate, having the constitution  $\text{CHR} \begin{smallmatrix} \text{CH}(\text{CO}_2\text{Alk})\cdot\text{CO}\cdot\text{CH}_3 \\ \text{CH}(\text{CO}_2\text{Alk})\cdot\text{CO}\cdot\text{CH}_3 \end{smallmatrix}$ . The mechanism of the process is generally supposed to consist in the initial formation of a compound of the aldehyde and the base which, it is usually stated, may be a primary or secondary but not a tertiary base; this initial compound then reacts with the ketonic ester, as, for example:



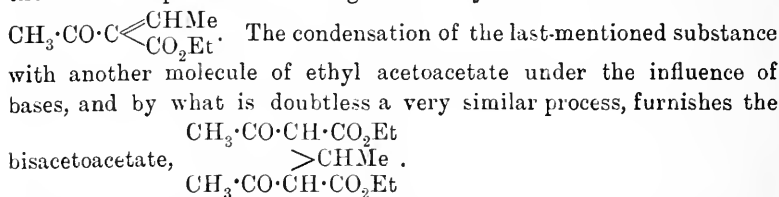
and Knoevenagel has isolated these supposed intermediate compounds and shown that they react with the acetoacetic esters in the manner represented in the foregoing equation (*Ber.*, 1898, 31, 2596).

The assumption that the condensation depends on the formation of such intermediate compounds is, however, entirely unnecessary, and the authors have found that, contrary to general belief, tertiary bases, if sufficiently powerful, are effective in bringing about the condensation, and there can be little or no doubt that the efficiency of a base depends mainly on its strength; thus, whilst pyridine scarcely acts at all, trimethylamine and tripropylamine in small quantities give good results, although they are not by any means so rapid in their action as the secondary bases, which are more powerful. In this and similar cases, the real effect of the bases is doubtless precisely similar to that which they exercise in bringing about the rapid attainment of equilibrium between the normal and *iso*-forms of tautomeric compounds, and in accelerating the union of hydrogen cyanide with carbonyl compounds, namely, by lowering the concentration of the hydrogen ions and thus increasing that of the negative ions of the acidic acetoacetic esters. The bases may be assumed to form small quantities of the ammonium derivatives exactly analogous to the metallic derivatives of the β-diketones or β-ketonic esters. The subsequent change may then be represented in the ordinary way as

the result of the addition of this ammonium compound to the carbonyl group of the aldehyde or more satisfactorily, we think, as the union of one of the ions\* of the acetoacetic ester with the carbonyl group of the aldehyde, to form a complex ion of the same type as that of the cyanohydrins (Trans., 1903, 83, 1000), followed by the union of these negative ions to form the hydroxyl compound (analogous to the cyanohydrins), which is generally recognised to be the first step in condensations of the type; thus with acetaldehyde and ethyl acetate,



the latter compound then losing water to yield the unsaturated ester



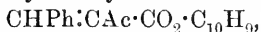
In the condensations of menthyl acetoacetate with aldehydes, the reactions appear to proceed more slowly than when the ethyl ester is used, and in many cases they are completed only after prolonged heating or by the addition of a small quantity of sodium hydroxide, which is very much more efficient than the comparatively weak organic bases.

\* We have previously suggested (Trans., 1902, 81, 1512) as a modification of an ionic view of tautomeric change which we supposed to have been advanced for the first time by Brühl (*Ber.*, 1899, 32, 2329), that the change of internal structure occurs only in the ions, as, for example, in the above case:



Brühl's paper, unfortunately, contained no reference to previous suggestions of a similar nature put forward by Knorr (*Annalen*, 1896, 293, 38) and by Wislicenus (*Tautomerie, Ahrens-Sammlung*, 897, *et seq.*). The latter had assumed, also, that ionisation might precede isomeric change, pointing out that when this was the case the change of internal structure would take place "more readily" than when an intramolecular atomic or group migration was also involved. Wislicenus thus anticipated a most important point in the views which we have put forward; he does not, however, appear to suggest that the change in the ion is a reversible one and tending towards an equilibrium (compare, in this respect, Lander, Trans., 1903, 83, 420), or that the ketonic form itself may undergo ionisation. The statement of the above view in terms of an hypothesis which does not postulate ionisation becomes virtually identical with Lander's suggestion (*loc. cit.*, p. 421) that the metallic derivatives exist in desmotropic forms.

The intermediate unsaturated esters, unlike those from the ethyl ester, may be occasionally produced in large amount by working at the ordinary temperature, and there is no difficulty in thus obtaining excellent yields of menthyl benzylideneacetoacetate,

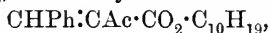


whilst in the preparation of the corresponding ethyl ester the temperature must be maintained below  $-5^\circ$  for more than 20 hours. The same remark applies to the condensation with propaldehyde, which at the ordinary temperature yields first the crystalline menthyl propylideneacetoacetate,  $\text{CHEt}:\text{CAc}\cdot\text{CO}_2\cdot\text{C}_{10}\text{H}_9$ , although none of the corresponding derivatives of ethyl acetoacetate with fatty aldehydes appear to be obtainable in a similar way. The want of success experienced in attempting to prepare other examples of these intermediate compounds is probably attributable to the failure of the substances to crystallise in the absence of suitable nuclei before they undergo further condensation. It is noticeable with nearly all the compounds dealt with that they crystallise with extreme sluggishness, this being a characteristic of the derivatives of menthyl acetoacetate which has already been mentioned on more than one occasion (Trans., 1902, 81, 1500, and 1903, 83, 1117). To this property also is doubtless due the failure which has attended all efforts to prepare crystalline condensation products from menthyl acetoacetate and formaldehyde. It is not our intention to discuss the moot question of the propriety of representing some of the alkylidenebisacetoacetates as derivatives of cyclohexanone, a contention which appears to involve the improbable assumption that the esters are more stable under the influence of hydrazine hydrate than under that of the trace of weak base which is usually employed in preparing them (compare Rabe and Elze, *Annalen*, 1902, 323, 83, and Knoevenagel, *Ber.*, 1903, 36, 2118). Moreover, the point has no very direct bearing on the interpretation of any of our observations.

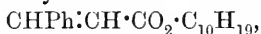
The menthyl esters of the alkylideneacetoacetic acids were not found to exhibit any very noteworthy mutarotation either in solvents or in the presence of traces of bases or acids. It is difficult to explain the reason for this apparent stability, more particularly as the specific rotatory powers of these esters are abnormally low, being in many cases not more than one-fourth of the value calculated from the observations of other workers on menthyl esters (Tschugaeff, *J. Russ. Phys. Chem. Soc.*, 1902, 34, 6069, and Cohen and Briggs, Trans., 1903, 83, 1213). In the absence of all other data, the abnormally low rotatory powers might have been reasonably attributed to the presence of an asymmetric carbon atom which originates in the acidic part of the molecule during the synthesis (compare Trans., 1903, 83, 1118), but the absence of any large amount of mutarotation,

such as was observed in the case of the azo-derivatives of menthyl acetoacetate, is difficult to reconcile with such a view.

Still more difficult to understand are the rotatory powers of the intermediate unsaturated alkylideneacetoacetates, which, if correctly represented by the formula  $\text{CHR}:\text{CAc}\cdot\text{CO}_2\cdot\text{C}_{10}\text{H}_{19}$ , contain no centre of asymmetry except that in the menthyl residue, nor, apart from the latter, is the molecule built up in an enantiomorphous way. Nevertheless, the rotatory powers of menthyl propylideneacetoacetate,  $\text{CHEt}:\text{CAc}\cdot\text{CO}_2\cdot\text{C}_{10}\text{H}_{19}$ , and benzylideneacetoacetate,



have the molecular rotations  $[\text{M}]_D - 97.70^\circ$  and  $-32.80^\circ$ , numbers which are respectively about two-thirds and one-fifth of the lowest usual values for the menthyl esters of monobasic acids, or, to look at the matter in another way, the latter of the two substances mentioned is apparently only the acetyl derivative of menthyl crotonate,



which has a rotatory power of about the normal value, namely,  $[\text{M}]_D - 203.1^\circ$  (*Annalen*, 1903, 327, 157). In view of these observations, Erlenmeyer may after all be correct in attributing an enantiomorphous character to one of the cinnamic acids (*Ber.*, 1903, 36, 2340. Compare also Sudborough and Thompson, *Trans.*, 1903, 83, 1167). The possibility still remains, however, that they may be re-

presented by the formula  $\begin{array}{c} \text{O} - \text{CMe} \\ | \quad | \\ \text{CHPh} \cdot \text{C} \cdot \text{CO}_2\text{Et} \end{array}$ , as, we believe, has already been suggested by Claisen.

## EXPERIMENTAL.

### *Methylene Derivatives.*

When molecular proportions of menthyl acetoacetate and formaldehyde, together with a few drops of piperidine, are allowed to remain for about twenty-four hours, condensation occurs with rise of temperature, water separates, and a colourless oil is obtained, which solidifies in the course of a few days. All attempts to obtain this substance in the crystalline form have been unsuccessful.

### *Ethylidene Derivatives.*

Numerous attempts were made to prepare *menthyl ethylideneacetoacetate* by condensing menthyl acetoacetate with aldehyde in alcoholic solution, but without success. The conditions were varied by using excess of the aldehyde and by keeping the mixture at  $0^\circ$  or  $-10^\circ$ ; in each case, however, the dimenthyl ester alone was formed.



This compound is best prepared by mixing two molecular proportions of the ester with one of acetaldehyde in alcoholic solution, a few drops of piperidine, diethylamine, or tripropylamine being added at intervals. The oily liquid is then warmed on the water-bath for two or three days, by which time it has assumed a jelly-like consistence, and contains the condensation product in the form of excessively slender needles. The mother liquors from these crystals on treatment with a drop of strong aqueous sodium hydroxide furnish an additional supply of material.

Some difficulty was experienced in obtaining the substance in a satisfactory condition; it was eventually found preferable to dry the compound thoroughly on a porous plate, then to dissolve it in cold dry benzene and precipitate with light petroleum.

0.1969 gave 0.5120 CO<sub>2</sub> and 0.1745 H<sub>2</sub>O. C = 70.9; H = 9.8.

C<sub>30</sub>H<sub>50</sub>O<sub>6</sub> requires C = 71.1; H = 9.8 per cent.

The compound is very readily soluble in all the usual media with the exception of water and light petroleum; it is obtained from a mixture of benzene and light petroleum in very slender, but well-formed, needles melting at 194—196°. The crystals have a weak double refraction; the extinction direction in polarised light is straight, and the directions of greatest elasticity and length are coincident. A solution of 0.4001 gram of the substance in 25 c.c. of benzene gave  $[\alpha]_D = -24.9^\circ$ , changing to  $-26.5^\circ$  on the third day.

Experiments were also made in order to determine whether the rotatory power was altered by the addition of a trace of a base as an accelerator. For this purpose, an approximately one per cent. benzene solution was divided between two 2-dcm. tubes, and a trace of piperidine added to one; the rotation in both cases, however, gave the same value, no mutarotation being observed during twenty-four hours.

### *Propylidene Derivatives.*

*Menthyl Propylideneacetoacetate*, CH<sub>3</sub>·CH<sub>2</sub>CH:C(CO·CH<sub>3</sub>)·CO<sub>2</sub>·C<sub>10</sub>H<sub>19</sub>

For the preparation of this compound, menthyl acetoacetate and propaldehyde in equivalent proportions were condensed with three or four drops of piperidine at the ordinary temperature. On the following day, the mixture formed a viscid, oily liquid containing drops of water, and was induced to solidify by the addition of a single drop of

concentrated aqueous sodium hydroxide, the flask containing the liquid being shaken vigorously from time to time. Condensation was also effected by allowing the reaction mixture to remain for some hours at  $0^{\circ}$ . In one experiment, two molecular proportions of menthyl acetoacetate were condensed with one of propaldehyde, the mono-menthyl ester being again formed. Another batch, prepared under the same conditions, yielded a compound melting at about  $200^{\circ}$ , which was subsequently shown to be the menthyl propylidenebisacetoacetate. Further condensations, however, whether effected with one or two molecular proportions of the menthyl ester only gave the unsaturated compound, the temperature at which the reaction proceeded being, apparently, immaterial.

0.2033 gave 0.5430  $\text{CO}_2$  and 0.1843  $\text{H}_2\text{O}$ .  $\text{C} = 72.8$ ;  $\text{H} = 10.0$ .

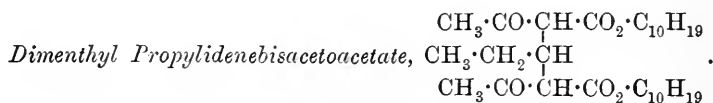
$\text{C}_{17}\text{H}_{28}\text{O}_3$  requires  $\text{C} = 72.8$ ;  $\text{H} = 10.0$  per cent.

The substance is easily soluble in benzene, chloroform, ether, or acetone, and when recrystallised from hot alcohol is obtained in the form of plates melting at  $84\text{--}88^{\circ}$ .

Conclusive evidence as to the nature of the compound under examination was afforded by its behaviour with warm sodium hydroxide solution, as a powerful odour of propaldehyde was evolved, and this decomposition is characteristic of the unsaturated alkylidene acetoacetates.

The crystals are rectangular, apparently orthorhombic plates which have straight extinction, the direction of greatest elasticity and length being coincident. The double refraction is strong. After melting between glass slips, this substance solidifies rapidly to fan-shaped masses which show aggregate extinction. Under the high power in convergent polarised light, the bisectrix of an interference figure of wide angle may be distinguished occasionally. The double refraction is positive, and the axial plane cuts the crystals in the directions of their greatest length.

The action of the substance on polarised light was investigated, 0.3980 gram being dissolved in benzene and made up to 25 c.c.; with this solution, a rotation corresponding with  $[\alpha]_D = -34.9^{\circ}$  was obtained, and no alteration of this value was observed.



This ester is obtained by condensing the monomenthyl derivative with about an equal weight of menthyl acetoacetate and a few drops of piperidine and alcohol. The reaction is considerably hastened by

warming on the water-bath, a viscid, oily liquid being obtained, which, on cooling, usually became almost solid in fifteen minutes.

0.1976 gave 0.5183  $\text{CO}_2$  and 0.1797  $\text{H}_2\text{O}$ .  $\text{C} = 71.5$ ;  $\text{H} = 10.0$ .

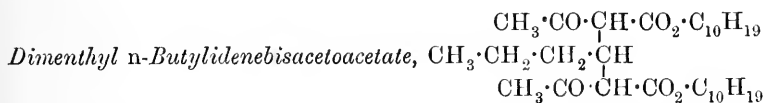
$\text{C}_{31}\text{H}_{52}\text{O}_6$  requires  $\text{C} = 71.5$ ;  $\text{H} = 10.0$  per cent.

The substance is easily soluble in benzene, chloroform, or hot ethyl acetate; very sparingly so in ether or light petroleum, and is almost insoluble in alcohol. On recrystallisation from acetone, it melts at  $201\text{--}207^\circ$ . The crystallographic characters of the compound are precisely similar to those of dimenthyl ethylidenebisacetoacetate.

A solution of 0.1301 gram in 25 c.c. of benzene had a constant rotation of  $[\alpha]_D = -26.9^\circ$ . Solutions in benzene in presence of a trace of piperidine were also observed in the polarimeter, but even here no mutarotation could be detected.

#### *Normal Butylidene Derivatives.*

All attempts to prepare menthyl *n*-butylideneacetoacetate were unsuccessful, the more complex ester being formed in each case.



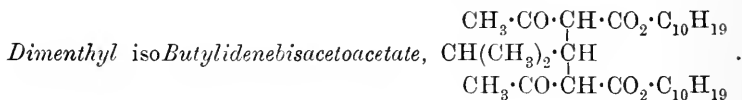
This substance is prepared by mixing *n*-butaldehyde with a molecular proportion of the menthyl ester in presence of a few drops of piperidine. The mixture soon forms an oily liquid at the ordinary temperature, and the product is obtained in the solid condition by the addition of alcohol and a small quantity of aqueous sodium hydroxide.

0.2023 gave 0.5339  $\text{CO}_2$  and 0.1853  $\text{H}_2\text{O}$ .  $\text{C} = 71.9$ ;  $\text{H} = 10.1$ .

$\text{C}_{32}\text{H}_{54}\text{O}_6$  requires  $\text{C} = 71.9$ ;  $\text{H} = 10.1$  per cent.

The compound separates from ethyl acetate in fine needles melting at  $184^\circ$ ; it is easily soluble in ether, benzene, and chloroform, less so in alcohol, acetone, and light petroleum. Crystallographically, it appears to be similar to the corresponding ethylidene derivative. A solution of 0.1857 gram in 25 c.c. of benzene gives  $[\alpha]_D = -16.8^\circ$ .

When this substance is treated in chloroform solution with hydrogen chloride, a viscid mass is obtained on evaporating the solvent; on triturating the substance with light petroleum and allowing the mixture to remain for some days, crystals are obtained melting at  $136.5\text{--}137.5^\circ$ , but this material was formed in such small quantity that it could not be subjected to detailed examination.

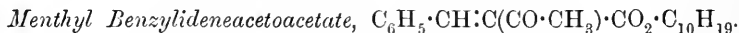
*isoButylidene Derivatives.*

This compound is obtained under conditions similar to those employed in the foregoing case, the addition of a drop of concentrated sodium hydroxide solution being used to hasten the condensation.

0.1647 gave 0.4331  $\text{CO}_2$  and 0.1500  $\text{H}_2\text{O}$ .  $\text{C} = 71.71$ ;  $\text{H} = 10.1$ .

$\text{C}_{32}\text{H}_{54}\text{O}_6$  requires  $\text{C} = 71.9$ ;  $\text{H} = 10.1$  per cent.

The substance crystallises from ethyl acetate in needles, which soften at  $193^\circ$  and melt completely at  $202^\circ$ . The ester is fairly soluble in the usual organic media; its crystals are slender needles, like those of the other alkylidenebisacetoacetates, but are always considerably larger and apparently somewhat better defined. A benzene solution of 0.2933 gram of the substance made up to 25 c.c. gave  $[\alpha]_D = -42.6^\circ$ ; here a slight mutarotation was observed, the rotatory power assuming a constant value of  $[\alpha]_D = -46.0^\circ$  at the end of a week.

*Benzylidene Derivatives.*

A mixture of menthyl acetoacetate and benzaldehyde in molecular proportion, together with a few drops of piperidine, was allowed to remain at the ordinary temperature for about 24 hours; a cloudiness, due to the separation of water, was noticed at the end of an hour, and a semi-solid mass was finally obtained. The crystalline substance which separated was freed from the remaining oil by filtration under pressure, and was then dried on a porous plate and recrystallised from hot spirit.

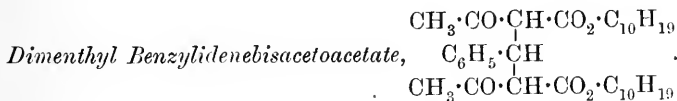
0.1960 gave 0.5491  $\text{CO}_2$  and 0.1487  $\text{H}_2\text{O}$ .  $\text{C} = 76.4$ ;  $\text{H} = 8.4$ .

$\text{C}_{21}\text{H}_{28}\text{O}_3$  requires  $\text{C} = 76.8$ ;  $\text{H} = 8.5$  per cent.

The compound is easily soluble in the usual organic media, although but sparingly so in light petroleum; it separates from alcohol in flattened, colourless needles, and melts sharply at  $133-134^\circ$ .

The crystals are well-formed, flat needles, or six-sided, elongated plates, which have straight extinction and are probably orthorhombic. The directions of greatest elasticity and length are coincident; the double refraction is moderate. When melted on a glass slip beneath

a cover-glass and then cooled, the compound solidifies fairly quickly in radiate masses of slender, flat needles, which are only distinguishable under a high power. A solution of 0.3995 gram of the substance in 25 c.c. of benzene gave  $[\alpha]_D = -10.0^\circ$ , no alteration in this value being noticed during three days.



This ester was obtained by condensing the benzyldene compound with one molecular proportion of menthyl acetoacetate in presence of a small quantity of alcohol and a few drops of piperidine; the mixture, when warmed on the water-bath, became considerably more viscous, and at the end of 12 hours was semi-solid and translucent. The product showed a great tendency to separate as a jelly from benzene, acetone, or ethyl acetate, but was obtained in the crystalline form by adding an equal bulk of light petroleum to its solution in cold chloroform; fine needles separated when the liquid evaporated at the ordinary temperature.

0.2077 gave 0.5612  $\text{CO}_2$  and 0.1720  $\text{H}_2\text{O}$ .  $\text{C} = 73.7$ ;  $\text{H} = 9.2$ .

$\text{C}_{35}\text{H}_{52}\text{O}_6$  requires  $\text{C} = 73.9$ ;  $\text{H} = 9.2$  per cent.

The compound is very sparingly soluble in alcohol, ether, and light petroleum, but dissolves fairly readily in benzene, acetone, or ethyl acetate. It softens at  $203^\circ$  and melts completely at  $206^\circ$ . Crystallographically, the substance resembles the corresponding ethylidene derivative. A solution of 0.1437 gram in benzene made up to 25 c.c. and observed in a 2-dm. tube gave a value for  $[\alpha]_D = -30.4^\circ$ .

*Addendum.*—It has been mentioned in the preceding pages that not only alkaline hydroxides and powerful primary and secondary organic bases, but also tertiary bases bring about the condensation of aldehydes with menthyl acetoacetate. This is found to be equally true with ethyl acetoacetate, as the following observations show.

When ethyl acetoacetate and 40 per cent. formaldehyde are mixed with pyridine even in fairly large quantity, no noticeable rise of temperature occurs, and condensation does not appear to take place even after some weeks at the ordinary temperature. If, however, two or three drops of concentrated trimethylamine solution or pure tripropylamine are added to 5 c.c. of the mixture, the temperature rises very rapidly, and in a few minutes water separates; in fact, these bases act much in the same way as does diethylamine, but considerably less rapidly weight for weight. As the products were liquid in the foregoing case,

a similar experiment was performed with a mixture of acetaldehyde (1 mol.) and ethyl acetoacetate (2 mols.); with 10 c.c. of such a mixture, 5 c.c. of pyridine produced no appreciable effect, but 20 drops of tripropylamine caused the separation of water within a few minutes at the ordinary temperature, and after three days the mixture solidified to a mass of crystals identical with those obtained by using piperidine or diethylamine in small quantities.

On adding 2 grams of tripropylamine to a mixture of 5.3 grams of benzaldehyde and 14 grams of ethyl acetoacetate, both freshly distilled, a marked rise in temperature occurred at once, and after five days at the ordinary temperature the whole had solidified to a crystalline mass of diethyl benzylidenebisacetoacetate.

We are indebted to the Research Fund Committee of the Chemical Society for a grant which defrayed a large part of the cost of this investigation.

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### VIII.—*Notes on some Natural Colouring Matters.*

By ARTHUR GEORGE PERKIN, F.R.S., and SAMUEL PHIPPS.

THIS investigation contains an account of the yellow colouring matters which are present in the flowers of *Prunus spinosa* and the Japanese dyestuff "Fukugi," together with some results which have been obtained during the further study of morin, myricetin, hesperitin, and curcumin.

#### *The Colouring Matter of the Flowers of Prunus spinosa.*

Some years ago, while examining the dyeing properties of certain natural products, it was noted that some quantity of yellow colouring matter exists as a glucoside in the flowers of *Prunus spinosa* or common blackthorn. A cursory examination carried out at the time resulted in the isolation of a product which was apparently a mixture, because its acetyl derivative did not melt sharply, the melting point being

very low for this class of substance. The attempts then made to effect a separation were not successful, but more recently, in the hope that a new colouring matter might be present, the subject has been again investigated, and the difficulty overcome in an exceedingly simple manner. In order to facilitate the work, an extract of these flowers prepared by Merck of Darmstadt was chiefly employed.

Two hundred grams of the extract dissolved in 2 litres of water were treated with 50 c.c. of hydrochloric acid, boiled for three hours, and, after cooling, extracted with ether to remove the colouring matter, which was thus obtained as a brownish-yellow, crystalline mass (3.5 grams). This was purified by two or three crystallisations from dilute alcohol, and a portion then converted into the acetyl compound in order to determine whether its melting point coincided with that of the corresponding derivative of some known substance of this class. It was found to melt somewhat indefinitely at 133—134°, and gave on analysis  $C=60.09$ ;  $H=4.28$ , these figures indicating that it was most probably a mixture. The main bulk of the colouring matter was now dissolved in a small quantity of boiling acetic acid, and the crystals which separated on cooling were collected and recrystallised from the same solvent until no alteration in the melting point could be observed; the yield was 0.8 gram.

Found  $C=62.93$ ;  $H=3.89$ .

$C_{15}H_{10}O_6$  requires  $C=62.94$ ;  $H=3.49$  per cent.

The substance, which consisted of pale yellow, glistening leaflets melting at 276°, dissolved in dilute aqueous alkalis with a pale yellow coloration.

The *acetyl* compound crystallised from methyl alcohol in colourless needles which melted at about 116°, resolidified at a higher temperature, and melted again at 181—182°.

Found  $C=60.77$ ;  $H=3.97$ .

$C_{15}H_6O_6(C_2H_3O)_4$  requires  $C=60.79$ ;  $H=3.96$  per cent.

On fusing the colouring matter with caustic alkali, phloroglucinol (m. p. 210°) and *p*-hydroxybenzoic acid (m. p. 208—210°) were obtained.

These facts, together with an examination of its dyeing properties, indicated without doubt that this colouring matter was *kampherol*. As this dyestuff has recently been found in at least four other plants, it is likely to occur in many other vegetable species.

The acetic acid mother liquors from which the kampherol had separated were allowed to absorb moisture by exposure to the

atmosphere, which caused the deposition of a small quantity of a mixture of a kampherol and a second substance. This precipitate was removed, the filtrate treated with a small quantity of hot water, and the yellow precipitate, which slowly separated, was collected and purified by conversion into its *acetyl* derivative.

Found C = 58.67 ; H = 4.26.

$C_{15}H_5O_7(C_2H_3O)_5$  requires C = 58.59 ; H = 3.90 per cent.

This substance, which melted at  $191^\circ$ , was decomposed with acid in the usual manner, and the regenerated colouring matter crystallised from dilute alcohol.

Found C = 59.56 ; H = 3.61.

$C_{15}H_{10}O_7$  requires C = 59.60 ; H = 3.31 per cent.

It formed glistening yellow needles soluble in alkali solutions with a yellow coloration ; on fusion with caustic potash, it gave phloroglucinol (m. p.  $210^\circ$ ) and protocatechuic acid (m. p.  $193-195^\circ$ ). It was evidently *quercetin*, and to this colouring matter and kampherol the dyeing property of these flowers is evidently due.

A cursory examination of the flowers of the violet (*Viola odorata*) and the white clover (*Trifolium repens*) by a method similar to that employed above indicated in each case the presence of *quercetin* in the form of a glucoside. This colouring matter was recognised by the melting point of its acetyl derivative, and its decomposition products with caustic alkali, and in consequence of these observations a fuller investigation appeared unnecessary.

### *The Japanese Dyestuff "Fukugii."*

We are indebted to the kindness of Professor E. Yoshitake, of Tokio, for this material, which consists of the wood of a tree, and was obtained in the form of an almost colourless, coarse powder ; it appears, at least until recently, to have been employed to a considerable extent as a yellow mordant dyestuff, principally in the form of extract. A preparation of this kind was also procured and consisted of brittle, rectangular cakes ( $4'' \times 2\frac{1}{2}'' \times 1\frac{1}{2}''$ ) of a yellowish-brown colour, which weighed approximately 410 grams.

The coarsely powdered extract, dissolved in ten times its weight of water, was boiled with 100 c.c. of hydrochloric acid for two hours in order to decompose the glucoside. A somewhat viscous precipitate of the impure colouring matter thus separated, which, when cold, was washed by decantation, drained on a tile, and allowed to dry at the ordinary

temperature. The product was extracted with boiling alcohol, the extract evaporated and poured into a large bulk of ether, which caused the separation of a resinous impurity, and on evaporating the ethereal liquid the colouring matter now obtained was of a much lighter colour. For further purification, it was dissolved in boiling alcohol containing a trace of acetic acid, lead acetate solution added, the resulting yellow precipitate removed, the filtrate evaporated to a small bulk and poured into ether. The pale yellow, ethereal liquid was well washed with water, evaporated to dryness, and the viscid residue left for some days. Minute crystals slowly separated, which were collected, washed with a small amount of ether, and crystallised first from dilute ethyl alcohol and then from methyl alcohol until the melting point was constant. The product frequently contained a trace of the lead compound, which adhered somewhat tenaciously, and was best removed by means of ether, in which it dissolved with difficulty.

Found, (i) C = 65.03 ; H = 4.04. (ii) C = 65.17 ; H = 3.97.

$C_{17}H_{12}O_6$  requires C = 65.37 ; H = 3.84 per cent.

It consisted of a mass of minute, prismatic, canary-yellow needles, which melted at 288—290°. When crystallised from dilute alcohol, the air-dried product contains one and a half molecules of water of crystallisation.

Found,  $H_2O = 7.56$ .

$C_{34}H_{24}O_{12} \cdot 3H_2O$  requires  $H_2O = 7.35$  per cent.

This new colouring matter, for which the name *fukugetin* is proposed, is readily soluble in hot alcohol and dissolves in aqueous alkalis or in cold sulphuric acid with a pale yellow coloration. The solution in the latter solvent, on heating, becomes dull violet-red, and finally assumes an orange-brown tint, and, on dilution with water, now deposits a brown, amorphous precipitate soluble in aqueous alkalis to a dull red solution. With lead acetate in alcoholic solution, an orange-yellow precipitate is formed, whilst alcoholic ferric chloride develops a brownish-black coloration ; on the other hand, alcoholic potassium acetate gives no insoluble salt, and mineral acids do not react to form the usual compounds. When examined by Zeisel's method, it was found to contain no methoxyl groups.

Fukugetin readily dyes mordanted fabrics, and it was at once observed that the shades produced were almost identical, except as regards the iron mordanted portion, with those given by luteolin.

	Cr.	Al.	Sn.	Fe.
Fukugetin.	Dull orange-yellow.	Orange-yellow.	Bright ye'llow.	Olive-brown.
Luteolin.	Brown orange-yellow.	„	„	Olive-black.

Crystalline acetyl and benzoyl derivatives of this new colouring matter could unfortunately not be obtained either by the usual processes or by the pyridine method. Methylation also led to the formation of a viscous product, although it is possible that these difficulties might have been surmounted if a larger quantity of substance had been available for experiment.

*Bromine Compound.*—One gram of fukugetin was added to a solution of one gram of bromine in a little glacial acetic acid. After twenty-four hours, the product was drained on porous tile, ground up with a small amount of acetic acid, filtered at the pump, washed once or twice with acetic acid, and purified by crystallisation from nitrobenzene, two or three drops of acetic acid being added to the solution when cooling. Two distinct preparations were made.

Found, (i) C = 43.47; H = 2.43. (ii) C = 43.53; H = 1.95.

$C_{17}H_{10}O_6Br_2$  requires C = 43.22; H = 2.54.

*Dibromofukugetin* forms minute, flat needles melting at  $280^\circ$ , readily soluble in hot alcohol, more sparingly so in acetic acid.

On fusion with alkali in the usual manner, fukugetin gave protocatechuic acid (m. p.  $194-196^\circ$ ) and phloroglucinol (m. p.  $210^\circ$ ).

The above results are, unfortunately, too meagre to allow of the prediction of the constitution of this substance with any certainty, but the similarity of most of the general properties of the compound with those of luteolin, and the fact that it contains similar nuclei, point to the probable close relationship between these colouring matters. Interesting in this respect is the stability of alkaline solutions of fukugetin when exposed to the air, for these do not undergo oxidation even after many days. This property, as shown in former investigations, is somewhat characteristic of flavone compounds such as apigenin and luteolin, but is not possessed by flavanol derivatives, of which fisetin and quercetin may be quoted as examples. It is possible that the distinction between luteolin and fukugetin consists chiefly in the manner by which the catechol nucleus is connected with the pyrone ring, and one or two formulæ suggest themselves as very probable representatives of this colouring matter. It is intended, should a further supply of raw material be forthcoming, to continue these experiments in the hope of elucidating with certainty the constitution of this interesting substance.

An examination of the dyeing properties of "fukugi" showed, as was to be expected, that it behaved in this respect in an analogous manner to weld (*Reseda luteola*). The similarity in shade was so marked that, except in point of strength—for fukugi is a stronger dye than weld—

it is impossible to distinguish between them, and there can be little doubt that prior to the introduction of the synthetical colouring matters this dyestuff would have been a valuable addition to those already in use.

### *Ethylation of Morin.*

Although quercetin and other members of the flavanol class readily give, on alkylation, well-defined crystalline substances, morin has only yielded a methyl ether in a state of purity (Trans., 1896, 29, 192), for on ethylation in the usual manner, viscous products result which have hitherto refused to crystallise. As it seemed possible that the impurities might be more readily removed after acetylation, the residue from former experiments carried out some years ago was treated in the following manner.

The resinous mass was digested with boiling acetic anhydride for some hours, the solution evaporated to a small bulk, and diluted with about twice its volume of methylated spirit. After several days, a small quantity of crystalline matter separated, and the mixture was now set aside for some weeks; the product was then collected, crystallised two or three times from methyl alcohol, and thus obtained in colourless needles, readily soluble in hot alcohol and melting at 121—123°.

Found, C = 65.70; H = 6.22.

$C_{15}H_5O_3(OEt)_4 \cdot C_2H_3O$  requires C = 65.78; H = 6.06 per cent.

To prepare the free tetraethyl ether, the acetyl compound was digested with boiling alcoholic potassium acetate, the solution poured into a small quantity of dilute hydrochloric acid and the product crystallised from methyl alcohol.

Found, C = 66.50; H = 6.63.

$C_{15}H_6O_3(OEt)_4$  requires C = 66.65; H = 6.28 per cent.

*Morin tetraethyl ether* forms pale yellow, prismatic needles, sparingly soluble in cold methyl alcohol, and melting at 126—128°. In general properties, it closely resembles the tetramethyl ether previously described (*loc. cit.*).

*The Bromination of Myricetin in the presence of Alcohol.*

A most interesting property of morin,  $C_{15}H_{10}O_7$ , the colouring matter of old fustic, is that when brominated in the presence of alcohol it yields tetrabromomorin ethyl ether,  $C_{15}H_5O_6Br_4 \cdot OEt$ . This peculiar behaviour, which is apparently not possessed by other flavanol derivatives, is considered by Herzig (*Monatsh.*, 1897, 18, 700) to render doubtful the constitution assigned to it by one of the authors (*Trans.*, 1896, 29, 792).

Being in possession of a small quantity of myricetin, which is apparently a flavanol derivative capable of yielding a tetrabromocompound (*Trans.*, 1896, 69, 1287), the authors have studied its behaviour in these circumstances.

Myricetin (1.9 grams) in 20 c.c. of alcohol was treated with 3.4 grams of bromine and the mixture left for forty-eight hours, when on cautiously diluting with water a small quantity of crystalline precipitate gradually separated and was recognised as tetrabromomyricetin (*loc. cit.*); this was removed after some hours, the filtrate treated with a large volume of water, and a second deposit collected and crystallised two or three times from dilute alcohol.

Found, C = 31.29; H = 1.68; Et = 4.36.

$C_{15}H_5O_6Br_4Et$  requires C = 30.81; H = 1.51; Et = 4.38 per cent.

*Tetrabromomyricetin ethyl ether* formed colourless needles very soluble in alcohol; it becomes red at  $110^\circ$ , commences to sinter at  $132^\circ$ , and melts with decomposition at  $146^\circ$ . This melting point is given with reserve, owing to the possibility that a trace of tetrabromomyricetin itself may be associated with the product. The lack of raw material did not permit of further experiment, but the result indicates that in these circumstances myricetin behaves in an analogous manner to morin, though somewhat less readily.

*The Molecular Weights of Hesperitin and Curcumin.*

In a previous communication (*Trans.*, 1898, 31, 1031), it was shown that the properties of hesperitin were in accord with the constitution  $OH \cdot C_6H_3(OCH_3) \cdot CH : CH \cdot CO \cdot O \cdot C_6H_3(OH)_2$ , previously indicated by Hoffmann (*Ber.*, 1876, 9, 685) and Tiemann and Will (*ibid.*, 1881, 14, 848). The fact, however, that this substance gave well-defined crystalline salts having the formulæ  $(C_{16}H_{14}O_6)_2C_2H_3O_2K$  and

$C_{32}H_{27}O_{12}K$  suggested that its molecular weight was  $C_{32}H_{28}O_{12}$ , or twice that assigned to it by these authors.

More recently it was shown (Trans., 1903, 88, 127) that certain substances, the molecular weights of which were well known, also gave somewhat peculiar salts by similar methods. Thus from gallacetophenone,  $C_8H_8O_4$ , the salt  $C_{24}H_{23}O_{12}K$ , and from daphnetin,  $C_9H_6O_4$ , the salt  $C_{18}H_{11}O_8K$  resulted, and other cases might be cited. It was accordingly evident that these salts do not in all cases furnish trustworthy indications of the molecular weight, and cryoscopic experiments were therefore carried out, advantage being taken of the ready solubility of acetylhesperitin in naphthalene.

0.3351 in 13.90 naphthalene gave  $\Delta t - 0.375^\circ$ . Found,  $M = 449$ .

0.4310 ,, 13.87 naphthalene gave  $\Delta t - 0.490^\circ$ . Found,  $M = 443$ .

$C_{16}H_{11}O_6(C_2H_5O)_3$  requires  $M = 428$ .

It is consequently evident that the molecular weight of hesperitin is represented by the formula  $C_{16}H_{14}O_6$ , and that the above-mentioned potassium and sodium salts belong to the class of "semi-substituted" compounds (*loc. cit.*).

It has been shown by Ciamician and Silber (*Ber.*, 1897, 30, 192) that the molecular weight of curcumin is most probably represented as  $C_{21}H_{20}O_6$  rather than  $C_{14}H_{14}O_4$ , the formula originally assigned to it by Jackson and Menke (*Amer. Chem. J.*, 1882, 4, 77). Analyses of its mono-potassium salt (*loc. cit.*), although agreeing approximately with the formula  $C_{21}H_{19}O_6K$ , were not completely satisfactory, owing to the difficulty of purifying this somewhat soluble compound. It therefore appeared interesting to confirm these results, if possible, by the cryoscopic method, for which purpose a benzoylcurcumin would probably be suitable.

This derivative was readily prepared by treating 2 grams of curcumin dissolved in 30 grams of pyridine with 23 grams of benzoyl chloride. The product was washed with water, the viscous residue dissolved in alcohol, and the crystals, which gradually separated, were purified by crystallisation from a mixture of this solvent and benzene.

Found,  $C = 73.87$ ;  $H = 4.48$ .

$C_{21}H_{17}O_6(C_7H_5O)_3$  requires  $C = 74.11$ ;  $H = 4.70$  per cent.

*Benzoylcurcumin* consists of fine, lemon-yellow needles melting at  $176-178^\circ$ .

0.3256 in 13.23 naphthalene gave  $\Delta t - 0.25^\circ$ . Found,  $M = 688$ .

$C_{21}H_{17}O_6(C_7H_5O)_3$  requires  $M = 680$ .

These results therefore indicate that the molecular weight assigned

to curcumin by Ciamician and Silber is correct, and point to the fact that this colouring matter contains three hydroxyl groups, although only two have hitherto been suspected.

Curcumin itself is somewhat soluble in naphthalene, but apparently not sufficiently so for molecular weight determination; the cryoscopic experiments gave  $M=429$ , whereas the formula  $C_{21}H_{20}O_6$  requires  $M=368$ .

The isolation of curcumin from turmeric is at best a tedious operation, and as the yields obtained by the published methods were not satisfactory, the following process was adopted.

An alcoholic extract of turmeric was treated with lead acetate solution (Daube, *Ber.*, 1870, 3, 709), and the precipitated lead compound of the colouring matter collected, thoroughly washed with alcohol, and then with water. The product suspended in warm water was decomposed with dilute sulphuric acid, and the resulting mixture of curcumin and lead sulphate well washed, drained on porous tile, and extracted with boiling alcohol. After concentration, the extract was poured into ether, the solution decanted from tarry matter, evaporated to a small bulk, and diluted with carbon disulphide. The mixture, when left exposed to the air at the ordinary temperature, gradually deposited crystals, which were collected from time to time, and in this way a yield of approximately 0.56 per cent. of curcumin was isolated from the sample of root employed. Little or no loss should occur by this process, and the mother liquors contain only a trace of the so-called turmeric resin.

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IX.—*The Four Optically Isomeric l-Menthylamines and their Salts.*

By FRANK TUTIN and FREDERIC STANLEY KIPPING.

IN the course of the investigation of the isomeric salts derived from hydrindamine (Kipping, Trans., 1903, 83, 873) and methylhydrindamine (Tattersall and Kipping, Trans., 1903, 83, 918), it seemed particularly important to try and obtain corresponding isomerides from some optically active base of a totally different type, and among such bases which are moderately accessible, menthylamine seemed to be the most suitable.

Two compounds, distinguished as *l*- and *d*-menthylamines, have been known for some time: *l*-menthylamine was obtained by reducing nitromenthene with zinc and sulphuric acid (Moriya, Trans., 1881, 39, 77), and also by reducing the oxime of *l*-menthone with sodium and alcohol (Andres and Andreef, Ber., 1892, 25, 609); *d*-menthylamine was prepared from the oxime of *d*-menthone (Andres and Andreef, loc. cit.), and was also obtained, together with the *l*-base, by heating *l*-menthone with ammonium formate (Wallach and Kuthe, Annalen, 1893, 276, 306); in the latter case, the two bases were separated by fractionally crystallising their formyl derivatives, which are the original products of the reaction.

These *l*- and *d*-bases, which are liquids, have been characterised by preparing from them a number of simple derivatives, and the specific rotations of many of the latter have been determined by Binz (Zeit. physikal. Chem., 1893, 12, 727).

Our investigations show that the base produced by the reduction of the oxime of "*l*-menthone" is a mixture of four optically isomeric menthylamines, in which, however, three of the bases are present in relatively very small quantities. The base obtained by the action of ammonium formate on *l*-menthone is likewise a mixture of these four optical isomerides, but apparently in proportions different from those in which they occur in the reduction product of the *l*-oxime.

The explanation of these facts is to be found in the origin and in the methods of formation of the basic mixtures. Leaving out of consideration the reduction of nitromenthene, the other methods for the preparation of the base start from menthone, a ketone which contains two asymmetric groups and which, in its turn, is produced by the oxidation of menthol with sulphuric acid and dichromate.

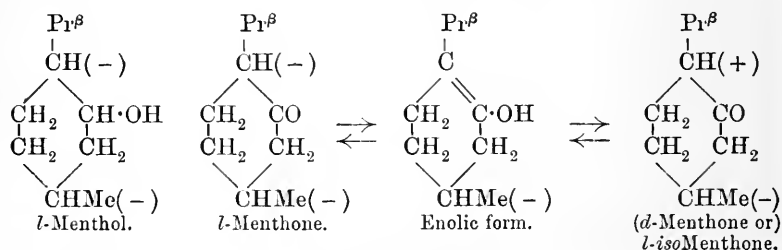
The menthone obtained by carrying out this oxidation with dilute sulphuric acid and dichromate at 30° has a specific rotation  $[\alpha]_D - 26^\circ$  to  $- 28^\circ$  and is called *l*-menthone; when, however, oxidation is accom-

plished with the aid of concentrated acid at  $30^{\circ}$ , the product has a specific rotation  $[\alpha]_D +26^{\circ}$  to  $+28^{\circ}$  and is called *d*-menthone, the "inversion" being due to the action of the concentrated acid (Beckmann, *Annalen*, 1889, 250, 322).

The application of the terms *laevo*- and *dextro*- to these two products and the observation that they have approximately equal but opposite specific rotations seem to have caused some confusion as to the relationship between these two ketones (compare Richter, *Organ. Chem.*, 1898, p. 340; Vorländer, *Ber.*, 1903, 36, 268). That they are not enantiomorphously related is indicated by the differences in physical properties and more especially by the values of the specific rotations of their oximes, both of which compounds are levorotatory, having specific rotations of  $[\alpha]_D -40.7^{\circ}$  to  $-42.5^{\circ}$  and  $-4.85^{\circ}$  to  $-6.67^{\circ}$  respectively.

That the conversion of "*l*-menthone" into "*d*-menthone" by the action of acids or of alcoholic solutions of alkalis is not an optical "inversion" but a partial racemisation is also rendered highly probable, even if not proved, by the fact that the product, "*d*-menthone," is optically active.

A consideration of the constitution of menthone leads to the same conclusion: assuming that the oxidation of menthol with dilute acid and dichromate gives one product only, then of the two asymmetric groups in this ketone which may be represented by — —, one only would probably undergo change under the influence of acids or alkalis, namely, that which is capable of keto-enolic tautomerism; the result would be a mixture, probably of unequal quantities, of the — — and — + isomerides, the formation of which may be indicated as follows:—



The values of the specific rotations of the partially racemised ketonic mixture would depend, therefore, on those of its two components and on the proportions in which they are present, and since it is quite possible that partial racemisation occurs to some extent even in the oxidation with dilute sulphuric acid and dichromate, ordinary "*l*-menthone" itself may be a mixture of the two optical isomerides.

Whether "*l*-menthone" is one definite compound or not, the oxime repared from it in the usual way in alkaline solution is doubtless a

mixture of the oximes derived respectively from the -- and - + ketones, and consequently, on reduction, since a third asymmetric group is produced, four optically isomeric menthylamines will be formed, as experiment shows, however, in very unequal quantities: these four isomerides would be the forms --- and - + - derived from the -- ketone, and -- + and - + + derived from the - + ketone.

Similar arguments hold good in the case of the formation of the base by heating menthone with ammonium formate; although there is here no free alkali, the high temperature would, no doubt, tend to give in the first place a mixture of two menthones, from each of which two menthylamines would then be produced; these four compounds would be identical respectively with those obtained from the oxime, provided that in both cases the asymmetric group containing the methyl radicle undergoes no change; were this group also to undergo inversion, then obviously four additional isomerides (+ - -, + + -, + - +, + + +) would be formed, and an optically inactive mixture of four externally compensated bases would be the final result. As we show later that all the four bases obtained in these reactions are optically active, it is proved that throughout all the changes involved in the production of menthylamine from menthol one of the asymmetric groups escapes racemisation.

*Nomenclature.*—If we assign to *l*-menthone the configuration --, then *d*-menthone would have the ++ configuration, and the ketone obtained from *l*-menthone by the action of acids or of alkalis would have the - + configuration, and might be named *l*-isomenthone. The two menthylamines derived from *l*-menthone may then be distinguished as *l*-menthylamine (---) and *l*-neomenthylamine (- + -); respectively (compare Forster, *Trans.*, 1898, 63, 391; Tattersall and Kipping, *ibid.*, 1903, 83, 919), those derived from the isoketone being named *l*-isomenthylamine and *l*-isoneomenthylamine respectively. The four isomerides derived from the true *d*-menthone (+ +) and from *d*-isomenthone (+ -) could then be distinguished in a similar manner.

We have adopted this system in dealing with the four bases described in this paper, and as the choice of the configuration originally assigned to any one isomeride is, of course, purely arbitrary, we retain the name *l*-menthylamine for the base produced in the largest quantity by the reduction of the oxime of "*l*-menthone" and assign to it the configuration ---.

One of the other three compounds undergoes partial racemisation, giving a base which is not *l*-menthylamine, and as the latter and the other two isomerides are stable, we infer that this partial racemisation takes place in the group  $>\text{CH}\cdot\text{NH}_2$ , which is known to change very

readily in some cases; if this is so, the base which undergoes change and that into which it is partially transformed would have the configurations  $--+$  and  $-++$ , since the  $-+-$  compound would give *l*-menthylamine. The two isomerides in question are therefore named the *l*-iso-bases, the unstable one being distinguished as *l*-isoneomenthylamine; the remaining compound is called *l*-neomenthylamine.

*Isomeric l-Menthylamine d-Bromocamphorsulphonates*.—Having obtained an optically pure *l*-menthylamine in sufficient quantity and having satisfied ourselves that the base did not undergo partial racemisation under the conditions of our experiments, we were able to study the question of the existence of isomeric salts; it was thus proved that *l*-menthylamine gives with the bromo-acid, isomeric salts corresponding with those obtained from hydrindamine and methylhydrindamine, but, as in some earlier cases, it seemed impossible to obtain the compound of lower molecular rotation in a pure condition, that is to say, free from its isomeride.

The separation of the four isomeric menthylamines already mentioned was accomplished by fractionally crystallising the hydrochlorides, *d*-bromocamphorsulphonates, *d*-camphorsulphonates, formyl and benzoyl derivatives in the manner indicated in the experimental part of this paper.

*l*-Menthylamine is isolated from the reduction product of menthone-oxime without much difficulty by either of the first two processes, but in order to separate the remaining mixture of isomerides none of the first four methods is sufficient, and it is necessary to convert the bases into their benzoyl derivatives, which are then submitted to a prolonged and troublesome process of fractional crystallisation. The bases are regenerated by hydrolysing their benzoyl derivatives with dilute sulphuric acid, but, unfortunately, in this process one of the isomerides (*l*-isoneomenthylamine) undergoes partial racemisation, giving the *l*-iso-base, so that we have been unable to obtain it, except in the form of its benzoyl derivative.

The following table shows the principal compounds which have been prepared:

	<i>l</i> -Base.		<i>l</i> -neo-Base.		<i>l</i> -iso-Base.		<i>l</i> -isoneo-Base.
	M. p.	$[\alpha]_D$ .	M. p.	$[\alpha]_D$ .	M. p.	$[\alpha]_D$ .	M. p. $[\alpha]_D$ .
<i>d</i> -Bromocamphorsulphonate	226° + 43·2°		70—75(?)	—	166° + 65°		—
<i>d</i> -Camphorsulphonate .....	158 - 5·3		188 + 11·8°		177 + 21·7°		—
Benzoyl derivative.....	156 - 61·9		128 - 17·4		121 + 22·7		104° - 3·8°

The specific rotations of the salts were determined in aqueous solutions, those of the benzoyl derivatives in chloroform.

## EXPERIMENTAL.

*Isolation of l-Menthylamine Hydrochloride.*

The base obtained by the reduction of the oxime of "*l*-menthone" with sodium and alcohol was distilled in steam, neutralised with hydrochloric acid, and the salt systematically crystallised from water; the most sparingly soluble portion consisted of coarse needles of *l*-menthylamine hydrochloride, the more readily soluble fractions, which were apparently mixtures, separated in more slender needles.

The specific rotation of the pure salt and those of the two most readily soluble fractions were determined with the following result: \*

<i>l</i> -Menthylamine hydrochloride.		Mixture of hydrochlorides.	
	$[\alpha]_D$ .		$[\alpha]_D$ .
Solvent, chloroform	-45.4°	-41.9°	} different samples.
" "	-45.6	-39.6	
" water.....	-36.6	-28.0	
	$[M]_D$ .		$[M]_D$ .
" " .....	-70.1	-53.5	

The value obtained in aqueous solution for the pure salt is rather higher than that obtained by Binz (*loc. cit.*), whose sample possibly contained an isomeride, the existence of which in the original reduction product is indicated by the lower specific rotations of the more readily soluble fractions.

*l*-Menthylamine *d*-Bromocamphorsulphonate,  
 $C_{10}H_{19} \cdot NH_2, C_{10}H_{14}OBr \cdot SO_3H$ .

The base from the most sparingly soluble hydrochloride (see above) gives, with *d*-bromocamphorsulphonic acid, a salt which crystallises readily in well-defined prisms melting at about 225°. When crystallised two or three times, this substance appears to be homogeneous and its melting point hardly changes appreciably, but, as will be shown later, it really consists of a mixture of salts, both, however, derived from pure *l*-menthylamine.

*l*-Menthylamine *d*-bromocamphorsulphonate is very sparingly soluble in ethyl acetate, sparingly so in water; it dissolves readily in alcohol or chloroform, but is practically insoluble in light petroleum.

The specific rotation of a sample which had been crystallised fifteen times from dilute alcohol was determined: in chloroform,  $[\alpha]_D + 48.5^\circ$ ; in water,  $[\alpha]_D + 43.25^\circ$ ,  $[M]_D$  being 201.5°.

\* In these and in all future optical determinations, unless otherwise stated, 20 c.c. of solution contained 0.5 gram of the substance.

Taking the molecular rotation of the bromocamphorsulphonic acid as  $[M]_D + 270$ , that of the base would be  $[M]_D - 68.5$ , a result which agrees closely with that deduced from the specific rotation of the hydrochloride.

*l*-Menthylamine *d*-Camphorsulphonate,  $C_{10}H_{19} \cdot NH_2 \cdot C_{10}H_{15}O \cdot SO_3H$ .

This compound, when prepared from the base contained in the pure *d*-bromocamphorsulphonate, crystallised in large needles melting at  $158^\circ$ ; it was moderately soluble in water, readily so in alcohol, and very soluble in chloroform; when deposited from aqueous solution, it contained water of crystallisation.

The specific rotation was determined with a sample of the dried salt: in chloroform,  $[\alpha]_D + 9.5^\circ$ ; in water,  $[\alpha]_D - 5.3^\circ$ ,  $[M]_D$  in the latter case being  $-20.5^\circ$ .

Taking the molecular rotation of the acid as  $[M]_D + 51^\circ$ , that of the basic ion would be  $[M]_D - 71.5^\circ$ , which is somewhat higher than the values previously obtained.

*Benzoyl-l*-Menthylamine,  $C_{10}H_{19}NH \cdot CO \cdot C_6H_5$ .

The benzoyl derivative, prepared from the pure bromocamphorsulphonate by the Schotten-Baumann method, crystallised from alcohol in large needles melting at  $156^\circ$ ; in chloroform,  $[\alpha]_D = 61.9^\circ$ .

*The Existence of Isomeric Menthylamines in the Reduction Product of "l-Menthoneoxime."*

Fractional crystallisation of the hydrochloride of the crude base, obtained by reducing *l*-menthoneoxime, gave, as already stated, products differing in specific rotation; the *d*-bromocamphorsulphonate, prepared from all the more readily soluble fractions of the hydrochloride, or from the original basic reduction product, proved to be a mixture, from which, by repeated crystallisation from dilute alcohol, we isolated (*a*) a salt melting at  $225^\circ$ , identical with pure *l*-menthylamine *d*-bromocamphorsulphonate; (*b*) a salt melting very indefinitely at  $170$ — $176^\circ$ , which was obviously a mixture, and the further treatment of which is described later.

The salt melting at  $225^\circ$  formed by far the greater proportion of the whole product, even when the *d*-bromocamphorsulphonate was prepared from the more readily soluble portions of the fractionated hydrochloride.

*The Formation of Isomeric l-Menthylamine d-Bromocamphorsulphonates.*

A considerable quantity of *l*-menthylamine *d*-bromocamphorsulphonate was prepared partly by the fractional crystallisation from dilute alcohol of the salt obtained from the pure hydrochloride, and partly in a similar manner from the crude *d*-bromocamphorsulphonate; when, judging by the melting point and crystalline form, it seemed that we had obtained a definite compound, the whole of the pure material was separated into six fractions, and the first and last were examined polarimetrically in chloroform solution; the first fraction gave  $[\alpha]_D + 48.5^\circ$ , whilst the last fraction had  $[\alpha]_D + 48.0^\circ$ .

As these two extreme fractions had practically the same specific rotation and melted simultaneously at  $224\text{--}225.5^\circ$ , it seemed that the salt was homogeneous; nevertheless, we rejected the last fraction and its mother liquors. The remaining salt was then decomposed with barium hydroxide, regenerated from its component acid and base in the usual way (compare *Trans.*, 1903, 83, 906), and the product systematically crystallised from dilute alcohol; after thus obtaining nine fractions, each of which had been crystallised several times, and all of which seemed identical, the melting points and optical properties of the first and last fractions were determined.

	M. p.	In water.		In chloroform,
		$[\alpha]_D$ .	$[M]_D$ .	$[\alpha]_D$ .
First.....	226°	+43.75°	203.8°	48.75°
Last.....	221	+38.8	180.8	42.8

These experiments afforded almost conclusive evidence of the existence of isomeric salts, but in order to establish this fact beyond all question the first fraction only was decomposed and regenerated from its components; the salt thus obtained, when repeatedly crystallised from aqueous alcohol, gave extreme fractions having the same melting points as before ( $226^\circ$  and  $221^\circ$ ), and the specific rotation  $[\alpha]_D$  of the last fraction was found to be  $+39.5^\circ$  in water and  $+43.1^\circ$  in chloroform, these results agreeing closely with those previously obtained. The last fractions (m. p.  $221^\circ$ ) from the two preparations were added together and the mixture crystallised six times from dilute alcohol; the first fraction then melted moderately sharply at  $222^\circ$ , and its specific rotation in chloroform was  $[\alpha]_D + 44.4^\circ$ .

In these results we have a complete analogy between the case of *l*-menthylamine and that of *d*-hydrindamine (*loc. cit.*) or *l*-methylhydrindamine (*loc. cit.*); in spite of its apparent purity, the salt melting at about  $221^\circ$  is undoubtedly a mixture and contains a considerable quantity of the isomeride melting at  $226^\circ$ , although it does not seem

probable that a complete separation of the two components could be accomplished even by further crystallisation of very large quantities of material.

*Attempts to Isolate other Isomeric Menthylamines.*

The salt melting indefinitely at 170—176°, which is obtained on crystallising from dilute alcohol the *d*-bromocamphorsulphonate of the base prepared by the reduction of "*l*-menthoneoxime," forms tufts of short, slender needles and has a specific rotation of  $[\alpha]_D + 50^\circ$  (approximately) corresponding with a molecular rotation of  $[M]_D + 233^\circ$  in aqueous solution. This substance had the characteristics of a mixture, and all attempts to isolate a pure compound by crystallisation from dilute alcohol were unavailing.

As the salt of *l*-menthylamine with Reychler's *d*-camphorsulphonic acid was found to crystallise very readily from water, a separation of the bases in this crude *d*-bromocamphorsulphonate was attempted with the aid of this acid. We therefore liberated the basic mixture and prepared the *d*-camphorsulphonate, which crystallised from water in needles; after several crystallisations, the most sparingly soluble fraction, when dried in the air, melted at 144—147°, but when dried at 100° for several hours it melted at 164—165°, this difference indicating water of crystallisation. As this fraction of the salt appeared to be pure, its specific rotation in water was determined with the following result:  $[\alpha]_D + 5.8^\circ$ ,  $[M]_D + 22.4^\circ$ . The molecular rotation of the base in this salt would therefore be  $[M]_D - 29^\circ$ , that of the acid being  $[M]_D + 51.0^\circ$ .

As we expected that the base would be "*d*-menthylamine," it appeared probable that this salt, in spite of its having been repeatedly crystallised, was really a mixture containing a considerable proportion of the salt of the *l*-base; it was therefore converted again into the *d*-bromocamphorsulphonate. On crystallising this salt from ethyl acetate containing a little chloroform, a further quantity of *l*-menthylamine *d*-bromocamphorsulphonate, melting at 225°, was separated. The residue then crystallised from aqueous alcohol in very slender, bulky needles melting at 164—167°, but after many further crystallisations it melted sharply and constantly at 170°, and appeared to be homogeneous. A sample thus prepared, when examined polarimetrically, gave  $[\alpha]_D + 63.5^\circ$  in aqueous solution, whence  $[M]_D + 295.9^\circ$ ; this value indicating the presence of a dextrorotatory base having the molecular rotation  $[M]_D + 26^\circ$ , whereas the value for "*d*-menthylamine," calculated from that of the hydrochloride examined by Binz, is  $[M]_D + 33^\circ$ .

Not feeling satisfied that this salt was derived from pure "*d*-menthylamine," and the quantity being too small for further crystallisation, we

prepared some base by heating *l*-menthone with ammonium formate, and hydrolysed the crude mixture of formyl derivatives directly with hydrochloric acid.

The base thus obtained was converted into the *d*-bromocamphorsulphonate, and this salt, although showing a great tendency to separate as an oil from its solution in dilute alcohol, was finally obtained in tufts of fine needles, which, after recrystallisation, melted at  $168^{\circ}$ , the melting point not being raised by further crystallisation. The specific rotation of this salt was determined with the following result: in chloroform,  $[\alpha]_D + 54.5^{\circ}$ ; in water,  $[\alpha]_D + 63.9^{\circ}$ ,  $[M]_D$  being  $297.7^{\circ}$ .

As the specific rotation of the salt melting at  $170^{\circ}$  obtained from the products of the reduction of the oxime was  $[\alpha]_D + 63.5^{\circ}$  in aqueous solution, it seemed as if this substance was a pure salt of a *d*-base, but when a sample was converted into the hydrochloride, which crystallised from water in needles melting at  $230$ – $232^{\circ}$ , and a fraction of this product was examined in aqueous solution, it was found to be optically inactive, whilst another fraction gave  $[\alpha]_D + 6.8^{\circ}$  in aqueous solution, and a third was levorotatory. A solution of the base in dilute alcohol prepared from a portion of the inactive hydrochloride was also examined and found to be inactive.

#### *Isolation of Four Benzoylmenthylamines.*

The base in the *d*-bromocamphorsulphonate melting at  $170^{\circ}$  is therefore a mixture, even after the exhaustive purification which it has undergone; this was proved in the following manner: the benzoyl derivative was prepared by the Schotten-Baumann method from both the samples of *d*-bromocamphorsulphonates melting at  $168$ – $170^{\circ}$  and having specific rotations of  $63.5^{\circ}$  and  $63.9^{\circ}$  respectively. When crystallised from alcohol, both preparations were found to be mixtures, and as the result of a prolonged and very troublesome process of fractional crystallisation four benzoyl derivatives were ultimately isolated in a pure condition.

(1) The most sparingly soluble fraction, which crystallised in long needles, melted at  $156^{\circ}$ , had  $[\alpha]_D - 61.9^{\circ}$  in chloroform solution, and was identical with the benzoyl derivative of *l*-menthylamine.

(2) A compound which crystallised in long, glistening leaf-like plates, melted at  $128^{\circ}$ , and had  $[\alpha]_D - 17.4^{\circ}$  in chloroform solution.

(3) A compound which crystallised in thick tufts of short, fine needles, melted at  $104^{\circ}$ , and had  $[\alpha]_D - 3.8^{\circ}$  in chloroform solution.

As this derivative was the most fusible isomeride and might therefore have been a mixture, it was recrystallised three times from

alcohol, and the specific rotation again determined in chloroform solution, was  $[\alpha]_D - 3.9^\circ$ , indicating that the substance is pure.

(4) The most readily soluble fractions gave a benzoyl derivative which crystallised in very long, slender needles, melted at  $121^\circ$ , and had  $[\alpha]_D + 22.7^\circ$  in chloroform solution.

During the fractional crystallisation of the benzoyl derivatives, it was observed that when the original solutions were allowed to evaporate spontaneously, short, thick prisms were obtained, together with needles; when, however, these apparently homogeneous prisms were recrystallised, they gave needles and the glistening plates of the benzoyl derivative melting at  $128^\circ$ . The proportions of these four benzoyl derivatives actually isolated from the crude mixture were approximately equal, but the compound melting at  $104^\circ$  was perhaps obtained in rather the largest quantity. The various mother liquors contained a very considerable fraction of the total material.

#### *Attempts to separate the Isomeric Formylmenthylamines.*

Having proved that the basic product of the reduction of "l-menthoneoxime," as well as that obtained by heating "l-menthone" with ammonium formate, is a mixture of at least four menthylamines, not easily separated through the agency of their benzoyl derivatives, and, moreover, having found that these benzoyl derivatives are hydrolysed only with great difficulty, it seemed desirable to try and isolate the four amines in the form of their formyl derivatives, especially as the latter were known to undergo hydrolysis with moderate ease, and could therefore serve for the preparation of the bases themselves with less chance of partial racemisation. A considerable quantity of formylmenthylamine was therefore prepared, and, instead of hydrolysing directly, the crude product was crystallised first from ether and then from ethyl acetate, from which it finally separated in well-defined, four-sided prisms melting at  $112-113^\circ$ . The melting point of this, the principal crystalline product, was constant, but the mother liquors deposited a small quantity of crystals melting at  $117^\circ$ ; when these two preparations were mixed together, the mixture melted at  $115^\circ$ . The two specimens were, therefore, not different substances, but the more sparingly soluble fractions (m. p.  $112-113^\circ$ ) probably contained a small quantity of another formyl derivative not easily removed by crystallisation.

#### *l-iso-Menthylamine.*

The solid formyl derivative (m. p.  $112-113^\circ$ ) was then hydrolysed with strong hydrochloric acid; the hydrochloride thus obtained, after crystallisation from water, melted at  $186-187^\circ$ . The base in this salt

was then combined with *d*-bromocamphorsulphonic acid, and the compound thus obtained crystallised from dilute alcohol in well-defined needles melting at 166°. The specific rotation of this salt was determined in aqueous solution and found to be  $[\alpha]_D + 65^\circ$ , whence  $[M]_D + 303^\circ$ ; this gives a molecular rotation of the base  $[M]_D + 33^\circ$ , a value which is identical with that calculated from the molecular rotation of the "*d*-menthylamine" hydrochloride described by Binz (*loc. cit.*).

The base from this most sparingly soluble fraction of the *d*-bromocamphorsulphonate gave a pure benzoyl derivative melting at 121°, but the most soluble portions of the *d*-bromocamphorsulphonate seemed impure, and when the base contained in them was converted into the benzoyl derivative, the latter on fractional crystallisation gave, in addition to the compound melting at 121°, a small quantity of the benzoyl derivative melting at 128°. The formyl derivative melting at 112—113° is, therefore, impure in spite of repeated fractional crystallisation, and apparently the best way of obtaining a pure base is to hydrolyse the formyl derivative and crystallise a salt prepared from the basic mixture. The salt of this base, *l*-isomenthylamine, with Reyhler's *d*-camphorsulphonic acid, was prepared for the purpose of comparison with the *d*-camphorsulphonate of the base obtained on hydrolysing the benzoyl derivative melting at 128° (p. 77). It was moderately soluble in water, crystallising in needles which, when dried at 100°, melted at 177°. The specific rotation of this salt in aqueous solution was determined and found to be  $[\alpha]_D + 21.7^\circ$ , whence  $[M]_D + 83.9^\circ$ , so that the calculated value for the base is  $[M]_D + 33^\circ$ .

#### *Further Examination of Formyl Derivatives.*

The ethereal mother liquors from the crystallisation of the formyl derivative were evaporated, and the brown, syrupy residue distilled under 12 mm. pressure. After some unchanged menthone had passed over, about two-thirds of the remaining liquid distilled at 208—215°, giving an almost colourless, highly refractive, viscous liquid, to which a small quantity of ethyl acetate was added, when a larger quantity of the formyl derivative, melting at 112—113°, was obtained than that which crystallised from the ethereal solution of the original substance. This product, when separated from an uncrystallisable residue, was hydrolysed with strong hydrochloric acid and the base converted into the *d*-bromocamphorsulphonate. This salt, which appeared highly impure, and only crystallised partially when kept for some time in a vacuum, was therefore converted into the benzoyl derivative, the latter being fractionally crystallised from alcohol.

Probably about 75 per cent. of this product consisted of the derivative melting at  $128^{\circ}$ , this being identical with that obtained in small quantity from the formyl derivative melting at  $112$ — $113^{\circ}$ , but some of the benzoyl derivative melting at  $121^{\circ}$  was also isolated, together with a small quantity of the isomeride melting at  $156^{\circ}$ .

The distillation was stopped when the temperature reached  $238^{\circ}$ ; the residue in the flask was hydrolysed and converted into the benzoyl derivative, which, on fractional crystallisation from alcohol, was found to consist chiefly of the derivative melting at  $156^{\circ}$ , and a smaller amount of the derivative melting at  $104^{\circ}$ , although the proportion of the latter was not nearly so large as that obtained before in the fractional crystallisation of the benzoyl derivatives from the crude mixture of formyl derivatives; this fact, and further evidence obtained later, seemed to show that the formyl derivative corresponding with this benzoyl derivative had partially racemised on distillation.

In all the experiments in which the bases obtained from the formyl derivatives were separated by means of their benzoyl compounds, the proportion of the benzoyl derivative melting at  $156^{\circ}$  was always less than that of the isomerides melting at  $128^{\circ}$  and  $121^{\circ}$ .

#### *Hydrolysis of the Benzoyl Derivatives.*

The preceding experiments show that it is practically impossible, or at least very difficult, to separate the four formyl derivatives present in the original mixture; the compound melting at  $112$ — $113^{\circ}$ , which is the only crystalline substance obtained in any quantity, serves for the preparation of one base only, namely, *l*-isomenthylamine.

We were therefore obliged to make use of the benzoyl derivatives for the preparation of the two remaining bases, and as it was necessary to prove that the bases did not racemise during hydrolysis, we reconverted them either into the benzoyl derivative or into some salt which had been previously shown to be homogeneous.

The benzoylmenthylamines do not hydrolyse appreciably when boiled for many hours with strong hydrochloric acid, and when dilute sulphuric acid (1 : 1) is used, the only basic product obtained is a small quantity of ammonia.

A sample of the benzoyl derivative of *l*-menthylamine was heated for 6—8 hours in a sealed tube at  $140$ — $160^{\circ}$  with strong hydrochloric acid and a small quantity of glacial acetic acid; at the end of this time, the benzoyl derivative was completely decomposed into benzoic acid and a quantity of tarry matter mixed with menthene and menthylamine. The base was combined with *d*-bromocamphorsulphonic acid, and as the salt thus obtained melted at  $224^{\circ}$  after recrystallisation, the base seemed not to have racemised.

Some of the pure benzoyl derivative of *l*-isomenthylamine (m. p.  $121^{\circ}$ ) was hydrolysed in a similar manner, and the base again converted into the benzoyl derivative, which still melted at  $121^{\circ}$ , thus indicating that racemisation had not taken place to any appreciable extent.

*l*-Neomenthylamine.

As the benzoyl derivative melting at  $128^{\circ}$  appeared to be derived from a base which had not hitherto been isolated, it was analysed to prove that it really was a menthylamine derivative.

Found, C = 78.80 ; H = 9.67.

$C_{17}H_{25}ON$  requires C = 78.76 ; H = 9.65 per cent.

This benzoyl derivative was then hydrolysed in the manner already described, but the base, which was isolated by distillation in steam, was obtained in very poor yield. The *d*-bromocamphorsulphonate prepared from the distillate was dissolved in dilute alcohol and the solvent allowed to evaporate, but the salt separated as an oil, although, when slowly evaporated in a vacuum desiccator, the solution deposited nodular masses, which, when dried at the ordinary temperature, melted at  $70-75^{\circ}$ . Since this salt could not be obtained in well-defined crystals from the ordinary solvents, it was decomposed with caustic potash, and the base, when distilled in steam and combined with Reychler's *d*-camphorsulphonic acid, yielded a salt crystallising from the concentrated aqueous solution in well-defined needles, which, after recrystallisation, melted constantly at  $188^{\circ}$ . This salt had the appearance of a pure substance, and as it was less fusible than the *d*-camphorsulphonates of either of the other two bases we concluded that racemisation had not taken place to any appreciable extent.

*l*-Neomenthylamine *d*-camphorsulphonate is moderately soluble in water, alcohol, or ethyl acetate, and dissolves very readily in chloroform ; it crystallises from water in a hydrated state. The specific rotation of this salt in aqueous solution was determined and found to be  $[\alpha]_D + 11.8^{\circ}$ , whence  $[M]_D + 45.7^{\circ}$ . This gives  $[M]_D - 6^{\circ}$  (approximately) for the molecular rotation of the base, the constant for the acid being  $[M]_D + 51.0^{\circ}$ .

*l*-isoNeomenthylamine.

The benzoyl derivative of *l*-isoneomenthylamine, melting at  $104^{\circ}$ , was hydrolysed in a similar manner, and the *d*-bromocamphorsulphonate of the base dissolved in dilute alcohol ; the salt crystallised in fine needles, but had the characteristics of a mixture, and after three recrystallisations melted at about  $169^{\circ}$  ; from the mother liquors,

tufts of needles were obtained, which, after recrystallisation, appeared less impure than the more sparingly soluble fraction and melted at about 157°.

The base contained in this apparently impure *d*-bromocamphor-sulphonate was again benzoylated; the product, after fractional crystallisation from alcohol, consisted principally of the original benzoyl derivative melting at 104°, but a certain amount of benzoyl *l*-isomenthylamine (m. p. 121°) was contained in the more readily soluble fractions. It therefore appeared highly probable that *l*-isoneomenthylamine had undergone change to a certain extent, and this evidence confirms that obtained previously in examining the distillation products of the formyl derivatives, but with the quantity of material at our disposal we were unable to obtain salts of the base free from its closely related isomeride.

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## X.—*Peroxyaminesulphonates and Hydroxylaminetrisulphonates (Sulphazilates and Metasulphazilates).*

By TAMEMASA HAGA, D.Sc.

PERHAPS the most interesting of the sulphazotised salts discovered by Fremy (*Ann. Chim. Phys.*, 1845, [iii], 15, 408) are the two which result from the oxidation of one or other of the potassium hydroximino-sulphates (hydroxylaminedisulphonates) in aqueous solution by either silver oxide or lead peroxide or some other reagent. One of these products is the very unstable salt which he named *sulphazilate*. This substance is remarkable for crystallising from its aqueous solution, which is of an intense bluish-violet colour, in brilliant golden-yellow needles, very slightly soluble in ice-cold water, but dissolving easily in hot water. It can seldom be preserved for any length of time, and gives a disagreeable odour to the skin, like that caused by manganates and ferrates. According to Fremy, it is easily fusible, but that is a mistake; it is the products of its decomposition which melt. The other salt, his *metasulphazilate*, is also sparingly soluble in cold water, but is colourless and has considerable stability. It crystallises in

rhombic prisms which are so well defined that Fremy describes the compound as being the most beautiful of all the sulphazotised salts. These crystals appear to be isomorphous with those of potassium 5/6-normal hydroximosulphate and the two salts can hardly be separated by crystallisation. Its solution is quite neutral and gives a precipitate with basic lead acetate only. Fremy expressed the composition of the sulphazilate by the formula  $\text{HO}_7\text{NS}_2\text{K}_2$  (here written with the atomic proportions now in use), which is only incorrect in including hydrogen (Claus). He gave the composition of the meta-sulphazilate correctly as  $\text{H}_6\text{O}_{23}\text{N}_2\text{S}_6\text{K}_6$ .

Claus (*Annalen*, 1871, 158, 205), who gave details for the preparation of the coloured salt by lead peroxide, proved that in its production from potassium 5/6-normal hydroximosulphate it is not necessarily accompanied by sulphate; he also demonstrated with tolerable certainty that it is the sole product of the oxidation; and found that it passed spontaneously into the colourless salt, together with a fixed quantity of sulphate and a gas which is apparently nitrous oxide (compare page 89 of this paper). He recognised the sulphonate constitution of both salts and gave to the coloured salt the name and formula 'oxysulph-

azotate,'  $(\text{SO}_3\text{K})_3\text{N} \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{N}(\text{SO}_3\text{K})$ , and to the white salt the name and

formula, 'trisulphoxyazoate,'  $\text{O}:\text{N}(\text{SO}_3\text{K})_3 \cdot \text{H}_2\text{O}$ , that is, with the nitrogen quinquevalent in both formulæ. It will be seen that, even empirically, these formulæ differ a little from Fremy's. Claus also sought for, and, as he believed, obtained, the primordial sulphazotised salt which he formulated at first as  $\text{SO}_2\text{NO}_2\text{K}$  (*op. cit.*, 213), and afterwards as  $\text{O}:\text{N}(\text{SO}_3\text{K})$  (*Ber.*, 1871, 4, 508). This would be the analogue of the 'trisulphoxyazoate,' with the nitrogen only trivalent; but the existence of this salt has since been disproved (*Trans.*, 1900, 77, 437).

Raschig (*Annalen*, 1887, 241, 223) having found that the white salt, in a boiling and feebly acid solution, may yield sulphate to the extent of two-thirds of its sulphur, along with, apparently, hydroxyaminosulphuric (hydroxylaminemonosulphonic) acid, has recognised that it behaves as a derivative of hydroxylamine. But because it does not decompose when in strongly alkaline solution, he will not allow that it is that base trisulphonated. He modifies Claus's two formulæ, writing that

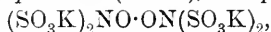
for the coloured salt as  $(\text{SO}_3\text{K})_2\text{N} \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{N}(\text{SO}_3\text{K})_2$ , and that for the white salt as  $(\text{SO}_3\text{K})_3\text{N} \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{N}(\text{SO}_3\text{K})_3 \cdot 2\text{H}_2\text{O}$ .

Hantzsch and Semple have found (*Ber.*, 1895, 28, 2744) that, when crystals of potassium 2/3-normal hydroximosulphate form in a bluish-

violet solution of potassium sulphazilate, they may contain 1—4 per cent. of this salt, apparently in solid solution, and consequently show a bluish-violet colour. These chemists have therefore advanced the view that Fremy's coloured salt, which they have renamed 'nitroxydisulphonate,' is sulphonated nitric peroxide, the yellow crystals of which have double the molecular magnitude of the dissolved bluish-violet form, in analogy with the two forms of nitric peroxide itself. The formula for the bluish-violet modification is given in a foot-note as  $\text{O}\cdot\text{N}\cdot(\text{SO}_3\text{K})_2$ , in which, therefore, the nitrogen is represented as being trivalent and the oxygen as univalent. A structural formula for the yellow modification is not given, but Raschig's is rejected, as having two quinquevalent nitrogen atoms in union with each other, a mode of combination which is without parallel. Raschig's formula for the white salt is also rejected, but as the simpler one proposed by Claus is adopted in its place, the quinquevalency of the nitrogen is maintained. On the authority of Schatzman, and as a result of their own experiments in the case of hydriodic acid, these chemists state that, in acting as an oxidising agent, the coloured salt reverts to hydroximinisulphate.

In 1896, Sabatier (*Compt. rend.*, 122, 1417, 1479, and 1537 ; 123, 255) published the results of an investigation of the violet solutions produced by the action of reducing agents on a sulphuric acid solution of nitrososulphuric acid, and suggested that the colour is due to the formation of the acid of Fremy's potassium sulphazilate. His suggestion is discussed on page 93 of this paper.

In the detailed examination of Fremy's sulphazotised salts made by Dr. Divers and the author, the results of which have been described from time to time in the Transactions, the sulphazilate and metasulphazilate were purposely reserved for separate treatment, because they are distinguished from the other salts in being products of oxidation. In the present paper, the author endeavours to prove (1) that the sulphazilate is an *oxime-peroxide* (Scholl), or a *peroxime*,



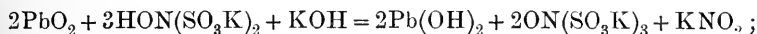
the first and only inorganic peroxime yet known ; (2) that the metasulphazilate is a *triacylated hydroxylamine*,  $(\text{SO}_3\text{K})_2\text{NO}(\text{SO}_3\text{K})$ , being the only compound of this type having an established normal constitution (all others, such as tribenzhydroxylamine, being apparently of more complex constitution) ; and (3) that, consequently, the nitrogen in both these sulphazotised salts is only trivalent, instead of being quinquevalent.

From among the several constitutional names which suggest themselves for Fremy's provisional 'sulphazilate' and 'metasulphazilate,' that of *peroxylaminesulphonate* for the former, and of *hydroxylamine-trisulphonate* for the latter, have been adopted as preferable. In

consequence, it has been found advantageous in this connection to call the parent salt *hydroxylaminedisulphonate*, instead of the alternative *hydroximinisulphate*, the name usually employed by Divers and the author. It has also been found convenient to treat of the hydroxylaminetrisulphonates before the peroxyaminesulphonates, from which they are apparently always derived.

*Hydroxylaminetrisulphonates (Metasulphazitates; Trisulphoxyazoutes).*

Potassium hydroxylaminetrisulphonate is most readily prepared by Fremy's method, in which there is no intermediate separation of its parent salt, the peroxyaminesulphonate. Somewhat alkaline potassium hydroxylaminedisulphonate is gently boiled and shaken with silver oxide or lead peroxide, until the solution, which at first becomes intensely bluish-violet, just loses its colour. Then, by evaporation and cooling, the filtered solution can be made to yield nearly all its hydroxylaminetrisulphonate. Theoretically, all the hydroxylaminedisulphonate should be converted into hydroxylaminetrisulphonate and nitrite,

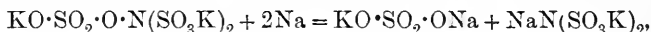


but sulphate and nitrous oxide are always produced, usually accompanied by very small quantities of nitrogen and aminemonosulphonate (aminosulphate). Nevertheless, 86 and 87·8 per cent. yields of the indicated quantity of the salt have been obtained, together with 78 and 85 per cent. of the full amount of nitrite as indicated by the urea method (p. 94). The production of such large quantities of the hydroxylaminetrisulphonate shows the inaccuracy of Claus's description of the changes concerned. According to that account, which is endorsed by Raschig, no nitrite is formed, and the utmost yield of hydroxylaminetrisulphonate would be equivalent to only 75 per cent. of the sulphur of the hydroxylaminedisulphonate.

*Constitution.*—Strictly speaking, the product of the triacylation of hydroxylamine with sulphonate radicles can only be a disulphonate, the third sulphonate radicle becoming sulphatic by its union with oxygen. But the name of hydroxylaminetrisulphonate is sufficiently appropriate for such a compound, since, although a sulphatic salt, it is not actually a sulphate, but a mixed anhydride of acid salts, one being the 2/3-normal hydroxylaminedisulphonate and the other the acid sulphate:  $(\text{SO}_3\text{K})\text{OH} + \text{HON}(\text{SO}_3\text{K})_2 = \text{H}_2\text{O} + (\text{SO}_3\text{K})\cdot\text{O}\cdot\text{N}(\text{SO}_3\text{K})_2$ . Lossen (*Ber.*, 1892, 25, 440) has already pointed out that dibenzhydroxamic acid may be regarded as the mixed anhydride of benzhydroxamic acid and benzoic acid, and similarly in the case of other diacylhydroxyl-

amines.\* Nitrososulphuric acid (nitrosyl hydrogen sulphate), the mixed anhydride of nitrous and sulphuric acids, is an example of a mixed inorganic anhydride. But the present salt, as the anhydride of two different acid salts, finds its close analogue in potassium hyponitrosulphate,  $(\text{SO}_3\text{K})\text{O}(\text{N}_2\text{OK})$  (Pelouze's "nitrosulphate," *Trans.*, 1895, **67**, 1098; 1896, **69**, 1610), which is the anhydride of an acid hyponitrite and an acid sulphate. The two mixed anhydrides agree in being stable in alkaline solution and unstable in acid solution, and in not giving barium sulphate with barium hydroxide or chloride.

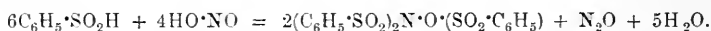
The evidence that the metasulphazilates have the constitution of hydroxylaminetrisulphonates is simple and direct, and similar to that as to the constitution of the hyponitrosulphates. In the first place, sodium amalgam decomposes them, apparently quantitatively (p. 96), into sulphate and normal aminedisulphonate (iminosulphate):



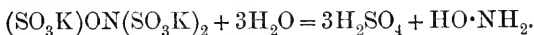
no sulphite being formed. Instead of sodium amalgam, the zinc-copper couple may be used to reduce hydroxylaminetrisulphonates in boiling solutions (p. 97), but in this case the aminedisulphonate is apt to hydrolyse during the heating. The result of this reduction of the salts not only proves their sulphatic constitution but shows also that neither the formula  $\text{ON}(\text{SO}_3\text{K})_2$  (Claus, Hantzsch) nor this formula doubled (Raschig) can possibly be right, because its acceptance would require that the sodium should act as a "carrier" of oxygen to the sulphonate radicle. Dunstan and Goulding (*Trans.*, 1899, **75**, 792) have found that trialkyloxamines, such as  $(\text{CH}_3)_3\text{N}:\text{O}$ , are reduced to trialkylamines by zinc and acid. Were metasulphazilates also oxaminic in constitution, they too should be reduced to aminetrisulphonates (nitrilosulphates). Sulphites, and even sulphur dioxide, have no action on the hydroxylaminetrisulphonates (p. 98).

In the second place, the metasulphazilates behave as sulphonated hydroxylamine. They reduce acidified permanganate; they give up one-third of their nitrogen in the form of ammonia when they are heated with soda-lime (Claus); and they can be hydrolysed ultimately into hydroxylamine and acid sulphate. Although very stable salts in other respects, they cannot, indeed, remain in solution very long or be

\* Twenty-six years ago, Koenigs (*Ber.*, 1878, **11**, 615 and 1588) found that benzenesulphinic and nitrous acids react to form hydroxylaminedibenzsulphinic (dibenzsulphydroxamic) acid, and that this with more nitrous acid becomes a tribenzsulphinic compound. Preliminary experiments made for the author seem to show that the latter will almost certainly prove to be hydroxylaminetribenzsulphinic acid. Its production may probably be expressed by the following equation:



kept for many months in the solid state without beginning to hydrolyse. But if a small amount of potassium or sodium hydroxide or, much more conveniently, of ammonia is added to their solution, they are permanent even for years in closed vessels. The other less sulphonated hydroxylamines have no such stability, but always revert more or less to sulphite and either nitrite or nitrous oxide. The hydrolysis is expressed by the equation :



Taking into consideration their water of crystallisation, the potassium and the ammonium hydroxylaminetrisulphonates can only be written with doubled formulæ, thus in some degree supporting Raschig's action in doubling Claus's formula for the former salt. But a cryoscopic measurement (p. 100) of the molecular magnitude of the sodium salt has shown that the simple formula is correct.

*Potassium hydroxylaminetrisulphonate*,  $2(\text{SO}_3\text{K})\text{ON}(\text{SO}_3\text{K})_2, 3\text{H}_2\text{O}$ , hitherto the only known salt, occurs in flattened, monosymmetric prisms, measurements of which have been made by Fock (Raschig). Its solubility in water at  $18^\circ$  is one in 25·37 parts. It is neutral to phenolphthalein, litmus, methyl-orange, and other indicators. When slowly heated to  $100$ — $120^\circ$  in the air, it loses some of its water of crystallisation, and is then hydrolysed by the remainder, acting together with the moisture of the atmosphere, so that at first it loses in weight and then gains. The residual mass is strongly acid, owing to the presence of acid sulphate. It has not been found possible to avoid hydrolysis and to obtain the anhydrous salt, even when the compound is very gradually heated in a current of dried air, after having already been exposed in a desiccator at the ordinary temperature. Its water, therefore, could only be determined by difference. As expressed by the foregoing formula, which agrees with Fremy's empirical formula, it is certainly  $3/2\text{H}_2\text{O}$ , although Claus made it out to be  $1\text{H}_2\text{O}$  only. In his paper, five concordant analyses of the anhydrous salt, besides four analyses of the hydrated salt, are given ; and so far from reference being made to any difficulty being experienced in rendering the salt anhydrous, it is stated that the water of crystallisation easily escapes at  $100^\circ$ . But it is important to note that his four determinations of the water give numbers which are all somewhat higher than those required by his calculation, although the salt occurs in large, clear, non-deliquescent crystals, and that the figures thus calculated are but little if any higher than those obtained by the author in two direct determinations of the loss of water by heating, in which the residues were always acid and therefore contained water. The salt has also been analysed by Raschig, but his results are not decisive (p. 99).

*Sodium Hydroxylaminetrisulphonate*,  $(\text{SO}_3\text{Na})\text{ON}(\text{SO}_3\text{Na})_2, 2\text{H}_2\text{O}$ .—This salt, now prepared for the first time, is obtained by boiling solution of 2/3-normal sodium hydroxylaminedisulphonate and its equivalent half-molecule of sodium hydroxide with lead peroxide. It is more difficult to purify from accompanying salts than the potassium salt, but by very cautious addition of sulphuric acid, these salts may be converted into sulphate, which can be easily separated from the hydroxylaminetrisulphonate by freezing. It crystallises in aggregates of small, tabular, monoclinic crystals (p. 99). The solubility of the salt is considerable, one part requiring only 2.83—2.85 parts of water at 21.5°. Like the potassium salt, it is neutral to indicators, and, when heated, hydrolyses in its water of crystallisation.

*Ammonium Hydroxylaminetrisulphonate*,  $\text{H}_{30}\text{O}_{23}\text{N}_5\text{S}_6$  or  
 $2(\text{SO}_3\text{NH}_4)\text{ON}(\text{SO}_3\text{NH}_4)_2, 3\text{H}_2\text{O}$ .

—The analysis of this salt confirms the view that the amount of water present in the potassium salt is greater than that found by Claus. The ammonium salt forms thick, rhombic plates and prisms, similar to those of the potassium salt and probably isomorphous with them. But goniometric examination was impracticable, for although some faces were 7—9 mm. long, others were too imperfectly developed for determination. The salt is neutral to litmus and methyl-orange, and generally like the potassium salt, but it is exceedingly soluble in water, one part dissolving in 0.61 part at 16°. The salt examined was prepared by digesting the basic lead salt with ammonium carbonate and evaporating the solution on the water-bath until it had almost lost its alkalinity, and then concentrating it further under reduced pressure over solid potassium hydroxide. Its nitrogen and sulphur were found to be in much closer agreement with the formula showing 3/2 molecules of water; but here again the difference between the numbers for the two formulæ is not very great (p. 100).

*Hydroxy-lead Hydroxylaminetrisulphonate*,  
 $\text{ON}(\text{SO}_3\text{PbO} \cdot \text{PbOH})_3, 3\text{H}_2\text{O}$ .

—This tetrabasic and very insoluble lead salt, which appears to be the only insoluble hydroxylaminetrisulphonate, was prepared by pouring a warm solution of the potassium salt into excess of carefully prepared basic lead acetate solution. It is a chalky powder readily decomposed by a solution of an alkali carbonate (p. 100).

*Peroxylaminesulphonates* (*Sulphazilates*; *Oxysulphazotates*; *Nitroxydisulphonates*).

Only silver oxide and lead peroxide have, as yet, been used in the preparation of a peroxylaminesulphonate, but many other oxidising agents produce the violet coloration, thus indicating the conversion of

a hydroxylaminedisulphonate into a peroxyaminesulphonate, as was pointed out by Fremy; even chlorine when used in limited quantity is able to produce this change. Ozone is an excellent reagent, rapidly producing a strong solution of the peroxyaminesulphonate when it is passed into a faintly alkaline solution of the hydroxylaminedisulphonate. Nitrous fumes are absorbed by an ice-cold solution of this salt, which assumes a dark-brown colour, and this solution, when rendered alkaline, slowly acquires the violet colour of the peroxyaminesulphonate. Also, when an ice-cold solution of potassium hydroxylaminedisulphonate and nitrite is barely acidified (preferably with sulphur dioxide), similar effects are produced. The temporary production of a violet colour is frequently observed in experiments made with the compounds of potassium nitrite and potassium hydroxylaminedisulphonates (Trans., 1900, 77, 432). Hydrogen peroxide, potassium ferricyanide, potassium permanganate, and alkaline cupric solutions do not interact with a hydroxylaminedisulphonate. Even freshly precipitated mercuric oxide has no action on it, although the oxide is more quickly affected by light when suspended in a solution of the salt.

In preparing potassium peroxyaminesulphonate, Fremy showed a preference for the use of silver oxide, whilst Claus, who assumed that the action of silver oxide was apt to proceed too far, preferred lead peroxide. Silver oxide gives a somewhat better yield and none of the silver goes into solution, whereas a little of the reduced lead peroxide dissolves and renders the salt impure. But the dissolved lead is readily removed, and the lead peroxide presents the advantage of being at hand when wanted, whilst the silver oxide has to be prepared each time and the metal afterwards recovered. Lead peroxide has therefore been used in the present research.

Fremy used either the  $2/3$ - or the  $5/6$ -normal potassium hydroxylaminedisulphonate as the source of the peroxyaminesulphonate; Claus used only the latter, and Raschig chose the former. The advantage lies with the  $5/6$ -normal salt, for, when prepared from a less alkaline salt, the peroxyaminesulphonate proves to be less easily purified and consequently less stable. The  $5/6$ -normal salt is always so far hydrolysed in dissolving that it is converted into the  $2/3$ -normal salt, the potassium hydroxide being left in solution, as noticed by Claus. The presence of free alkali, however, moderates the action of the oxidising agent, and to such an extent that a sufficiently concentrated solution of the very soluble normal sodium hydroxylamine-disulphonate is not attacked at all by lead peroxide. Apparently, therefore, lead peroxide acts as an acid oxidiser, in the form of plumbic anhydride, as suggested by Fremy.

The salt, which must be prepared just when it is wanted, is produced by mixing about 6 grams of the  $5/6$ -normal hydroxylaminedisulphon-

ate (or the same amount of the 2/3-normal salt together with a small quantity of potassium hydroxide) and a little more than the same weight of lead peroxide (or of the silver oxide precipitated from a little less than the same weight of silver nitrate) and making up with water to 25 c.c. The mixture is agitated for 15 minutes in water near to, but not above, 40°. Then the solution is decanted without delay, treated with carbon dioxide (when lead peroxide has been used), and filtered, before crystallisation sets in. The solution should therefore be kept warm up to this point. When it has remained some hours in an ice-box, almost the whole of the peroxyaminesulphonate will have separated as a crust of minute, yellow needles. These can be recrystallised, but not without material loss, from hot water made slightly alkaline with potassium hydroxide. When, as appears to have been the case with Fremy, much hydroxylaminedisulphonate has been left unoxidised, some of this will be found with the peroxyaminesulphonate, from which it can hardly be wholly separated by recrystallisation, its crystals remaining coloured by the peroxyaminesulphonate, as observed by Hantzsch and Semple.

Any close determination of the yield cannot be made directly, since the salt can rarely even be roughly weighed before decomposition sets in. Its amount has therefore to be estimated by letting it decompose, igniting the residue with ammonium carbonate, and weighing the potassium sulphate. In this way, the yield of separated salt was found to be a very little over three-fourths of the calculated quantity when silver oxide was used; and a little less than two-thirds when lead peroxide was taken. But by indirect means the amount of the salt actually produced can be shown to be much higher than this. As already mentioned (p. 81), the exhaustive oxidation by lead peroxide of a hot solution of hydroxylaminedisulphonate has given nearly 88 per cent. of the calculated quantity of hydroxylaminetrisulphonate, a fact which signifies that at least as much peroxyaminesulphonate as is equivalent to this percentage of the total sulphur must have been formed, since its production is intermediate to that of the hydroxylaminetrisulphonate.

Potassium peroxyaminesulphonate is very unstable in water and very slightly soluble in the cold. In *N*/10-solution of potassium hydroxide, which fairly represents its usual mother liquor, it is more stable, but still not very soluble; 100 parts at 3° dissolve only 0.62 part of the salt, and at 29° only 6.6 parts (p. 101). It interacts in solution with normal potassium sulphite and then produces hydroxylaminetrisulphonate and hydroxylaminedisulphonate, evidently in molecular proportions (p. 101), this change being a fact of great theoretical importance. Its chemical activity is manifested in oxidising certain easily oxidisable substances and being thereby reduced to its parent

salt, hydroxylaminedisulphonate. Although it liberates iodine from hydriodic acid, it fails to oxidise hydrochloric acid. When the latter acid in concentrated solution is poured on the solid salt, it sets up the same decomposition as that which occurs spontaneously (p. 88). But here, as the rise of temperature is moderated, definite although minute quantities of aminemonosulphonate and of hydroxylamine (not its sulphonate) can be found. The salt has practically no action on alcohol; nitrous and sulphurous acids rapidly reduce it, so also does sodium amalgam, first to hydroxylaminedisulphonate (as already observed by Schatzman), and then this salt passes slowly but completely into aminedisulphonate (iminosulphate). Clean granulated zinc slowly reduces the salt, but copper does not. The spontaneous decomposition of the salt may, however, easily be mistaken for its slow reduction by a reducing agent, since in this case also, as will be presently described (p. 89), hydroxylaminedisulphonate is produced. The difference is readily detected by testing for nitrite, which is produced only in the spontaneous decomposition of the salt. Manganese dioxide very slowly decomposes it, causing a minute effervescence; lead peroxide is inactive. Potassium permanganate is reduced to green manganate. Clean filter-paper, unlike the paper in use in Fremy's time, does not affect it.

Part of the instability of peroxyaminesulphonates must be attributed to the presence of oxidisable impurities. Thus, Fremy noticed the decomposing action of atmospheric dust; whilst nitrite, another impurity liable to be found in the salt, also greatly increases its instability. Acids hasten the decomposition of the salt; alkalis retard it. When drained on the tile from an alkaline solution, the salt may, under cover, remain undecomposed for two hours or more; but if washed on the tile and thus deprived of the traces of its adherent alkaline mother liquor, it will decompose in a very few minutes. Nevertheless, on one occasion some of the salt thus purified was kept on a tile for 11 months in a desiccator, and only then decomposed through an accident. This, however, must be regarded as a very uncommon experience. The sensitiveness of potassium peroxyamine-sulphonate to acids has been recorded by others, but has been somewhat exaggerated. When the salt is free from every trace of nitrite, its cold acidified solution may remain coloured for 40 minutes. An alkaline solution may not lose all its colour when kept in a closed vessel for more than a month. If sufficiently pure, the solid salt may be preserved for a day or so under water rendered slightly alkaline with potassium hydroxide.

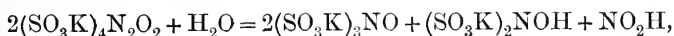
The nature of the decomposition of potassium peroxyaminesulphonate occurring in the absence of alkali has already been examined, although in all cases very imperfectly, by Fremy and by Claus, and in

the presence of alkali by Raschig. According to Fremy, the solid salt decomposes explosively when heated; when exposed to the air, it becomes strongly acid; and when heated in solution, it yields sulphate and a gas mistaken by him for oxygen, but which was really nitrous oxide. He was also mistaken in stating that it melts readily and that when left in a closed bottle it evolves nitric oxide. Claus found that, whether in the solid state or in solution, whether when cold or moderately heated, the decomposing salt yields hydroxylaminetrisulphonate and nitrous oxide, together with acid sulphate equivalent to one-fourth of its sulphur, according to the equation  $2K_4N_2S_4O_{14} + H_2O = 2KHSO_4 + 2K_3NS_3O_{10} + N_2O$ . Raschig has confirmed Claus's statements and also states that the solid salt or its solution also decomposes in this way even when left in contact with alkali. He also adds that its solution when acidified is decolorised in a few minutes, whilst in the presence of alkali it can in some cases be heated to boiling without change. All these statements by Claus and Raschig require to be modified in order that they may accurately describe the behaviour of the salt, and even then they fail to indicate the primary change which the decomposing salt undergoes. Thus the acid sulphate produced is seldom equal to one-fourth of the total sulphur, although it may be so, as twice found by Claus, and indeed also in the present investigation, but only when the salt had been used with too small a quantity of water to dissolve it all on warming. Owing to this fact, only a part of the nitrogen, which does not become hydroxylaminetrisulphonate, appears as nitrous oxide, along with a small amount of free nitrogen.

Solid potassium peroxyaminesulphonate is too unstable when dry and free from alkali to exist many minutes without rapidly and almost explosively decomposing. In this decomposition, slight white fumes of ammonium salt (probably pyrosulphite and pyrosulphate), nitrogen and nitrous oxide, and a small quantity of sulphur dioxide are given off, whilst the residue, when the mass of the salt has been at all considerable, gets very hot (above  $300^\circ$ ?) and melts. This residue consists of potassium sulphate (principally pyrosulphate) with a very little ammonium salt. Sometimes a trace of amine-monosulphonate can be detected by the mercuric nitrate test; also a trace of hydroxylamine (or other substance reducing alkaline cupric solution), but none of the other sulphonates, the temperature having been too high to leave these substances undecomposed.

The true products of the spontaneous decomposition of a peroxyaminesulphonate are only found (in company with small quantities of apparently secondary products) when the salt is heated to boiling with enough water to dissolve it, and in presence of sufficient alkali to prevent both the acidification of the solution during the decomposition

of the salt and also the secondary changes which would result from acidification. The alkali does not appear to modify the nature of the primary change, although it distinctly increases the stability of the salt, as already mentioned (p. 87). When carried out in the foregoing manner, the decomposition of a peroxyaminesulphonate proceeds largely in such a way that not only do three-fourths of the sulphur of the salt, as suggested by Claus and by Raschig, together with one-half of its nitrogen, come out as hydroxylaminetrisulphonate, but the rest of the sulphur and one-fourth of the nitrogen become hydroxylaminedisulphonate again, whilst the remaining one-fourth of the nitrogen appears as nitrite,



although some nitrous oxide and sulphate, besides minute and uncertain quantities of other substances, are always produced (p. 92).

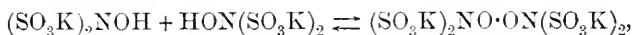
This result explains the production of the large quantities of acid sulphate and nitrous oxide observed by Claus and Raschig, for the nitrous acid when not neutralised by alkali interacts with the hydroxylaminedisulphonate and yields acid sulphate and nitrous oxide (Trans., 1900, 77, 433).

The regeneration of hydroxylaminedisulphonate in the spontaneous decomposition of a peroxyaminesulphonate accounts for the fact, met with in the present investigation, that much more hydroxylaminetrisulphonate is obtainable by heating hydroxylaminedisulphonate in solution with excess of lead peroxide than can be derived from the decomposition (out of contact with lead peroxide) of the peroxyaminesulphonate equivalent to that quantity of hydroxylaminedisulphonate (p. 81). For in the presence of lead peroxide, that hydroxylaminedisulphonate which is regenerated by the independent decomposition of the peroxyaminesulphonate is oxidised again to more of this salt, to be again decomposed in the same way, until the whole of the disulphonate has become trisulphonate and nitrite, except that part of it which is lost as sulphate and nitrous oxide. Remembering that  $4(\text{SO}_3\text{K})_2\text{NOH}$  gives  $2(\text{SO}_3\text{K})_4\text{N}_2\text{O}_2$ , the larger yield of hydroxylaminetrisulphonate which should result will be seen, on comparing the equation on page 81 with that just given, to be theoretically in the ratio 4:3. It will now, too, be evident, on reference to Claus's memoir, that his incomplete knowledge of the nature of the decomposition of the peroxyaminesulphonate led him to object too much to Fremy's account of the action of the oxidising agent in producing hydroxylaminetrisulphonate.

*Constitution.*—The constitution of a peroxyaminesulphonate as a sulphonate was recognised by Claus, and is deducible from the fact that it is formed by the dehydrogenation of hydroxylaminedi-

sulphonate. The problem of its constitution as a nitroso-compound remains to be solved, and the description just given of the potassium salt amounts to a demonstration, first, that its constitution is that of a peroxide and therefore of a peroximide; and, secondly, that its nitrogen is trivalent.

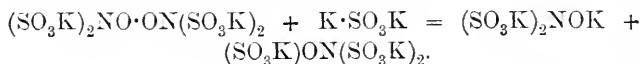
Among the facts bearing on its constitution as a peroxyamine, that is, as a derivative of  $\text{H}_2\text{NO}\cdot\text{ONH}_2$ , are, first, those of its mode of formation. The 2/3-normal hydroxylaminedisulphonate loses its two hydrogen atoms, at the ordinary temperature and when it is in aqueous solution, by the action of ozone, lead peroxide, silver oxide, and a variety of other substances:



but not, however, by oxygen itself; for Raschig's observation, that a solution of hydroxylaminedisulphonate when exposed to the air may assume a slight violet colour, applies in reality only to the case where the 2/3-normal salt is contaminated with nitrite, the pure salt never oxidising nor colouring in this way. The interaction with lead peroxide points clearly either to the peroxide constitution or, but with much less probability, to a rise in the combining power of the nitrogen to quadrivalency.

The fact of the ready reversion, at the common temperature and in solution, of a peroxyaminesulphonate to a hydroxylaminedisulphonate by acting as an oxidising agent is equally strong evidence of the same constitution. This reversion is also quantitative to an extent that admits of its being used to estimate the amount of the salt present in a solution (Schatzmann, Hantzsch and Semple).

Its combination with a molecule of normal sulphite (p. 86) affords convincing evidence to the same effect, since it is effected through the oxygen atoms of the peroxyaminesulphonate:



This interaction will be again discussed on page 91. Inferentially in favour of the peroxide constitution are also the odour which the peroxyaminesulphonates impart to the skin, their colour, and their decomposition into nitrous acid and sulphonated hydroxylamines.

So soon as it is recognised that peroxyaminesulphonates are peroxides, all doubt is removed as to the valency of their nitrogen, which then can be only that of a triad. Contrariwise, when such a constitution is not admitted, the nitrogen of a peroxyaminesulphonate, with equal certainty, cannot be trivalent. In order, therefore, to strengthen the conviction that the peroxyaminesulphonates are indeed peroxides and peroximides, it becomes important to state the

reasons against admitting the nitrogen of these salts to be quadrivalent or more than trivalent.

To begin with, it is extremely improbable that oxidation by lead peroxide, silver oxide, or ozone should raise the valency of the nitrogen to only quadrivalency and not to quinquevalency, and that it should raise it at all without converting the sulphonate to sulphate radicles. Neither Claus nor Raschig assumes that it does, for according to them the nitrogen of the hydroxylaminedisulphonate is itself quinquevalent. But there are also two strong reasons for rejecting the assumption that the valency of the nitrogen is raised by the oxidation of hydroxylaminedisulphonates to peroxyaminesulphonates. One of these is the nature of the products of the spontaneous decomposition of a peroxyaminesulphonate. These products, in so far as they contain nitrogen, are all trivalent nitrogen compounds, namely and in the main, hydroxylaminetrisulphonate, hydroxylaminedisulphonate, and nitrite; if nitrous oxide is also recognised, that fact will not affect the argument. No nitrate can be found among these products (p. 102). It is, of course, the establishment of the trivalency of the nitrogen of the first-named product which has really settled the matter. But as it is only as yet on the chemical work of Divers and the author (*Trans.*, 1894, 65, 523), that the adoption of the trivalency of the nitrogen in hydroxylaminedisulphonates can be based, the result of a determination by a cryoscopic method (p. 100) of the molecular magnitude of the normal sodium hydroxylaminedisulphonate may be adduced in support of it. This result shows that the molecule of the salt contains but one atom of nitrogen (necessarily, therefore, trivalent), and not two atoms as had been represented by Claus and by Raschig. Now, the spontaneous decomposition of a peroxyaminesulphonate can only be hydrolytic, and is therefore one not affecting the valency of the nitrogen; or, should this be contested, it can still be asserted that at least this decomposition cannot be interpreted as a change involving a diminution in the valency of the nitrogen.

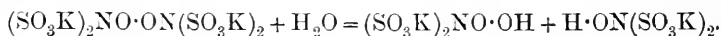
The other reason against the belief that the valency of the nitrogen changes when a hydroxylaminedisulphonate is oxidised to a peroxyaminesulphonate is that of the production of the two compounds of trivalent nitrogen, the hydroxylaminedisulphonate and hydroxylaminetrisulphonate, by the union of a peroxyaminesulphonate with a normal sulphite (p. 86). These two reasons for regarding the nitrogen of a peroxyaminesulphonate as trivalent seem to be conclusive, and therefore support the view that these salts are constituted as peroxides or peroximides.

Since the sodium salt is even more unstable than the potassium salt, the determination of the molecular weight of a peroxyaminesulphonate has not been possible. It would seem better to modify

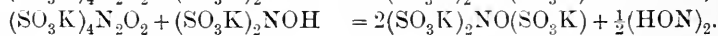
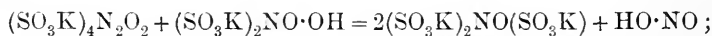
Hantzsch and Semple's suggestion concerning the molecular weights of the two forms of the potassium salt (p. 80), to the extent of giving the simple formula,  $(\text{SO}_3\text{K})_4\text{N}_2\text{O}_2$ , to the violet form, and reserving the double formula, or even a higher multiple of this, for the yellow form.

*Products of Decomposition.*—Without further experiments than those described on pages 94 and 106, the number of the products and the great variations in their proportions are such that the nature of the spontaneous decomposition of a peroxyaminesulphonate cannot yet be fully determined. But its general character can be indicated, now that the constitution of both peroxyaminesulphonates and hydroxylaminetrisulphonates has been determined.

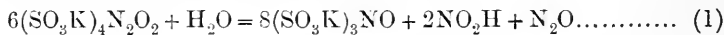
It can hardly be doubted that the molecule of peroxyaminesulphonate becomes halved by hydrolysis and converted into the hydroxylaminedisulphonate, always found in abundance, and the *hydroperoxyaminesulphonate*, as yet undiscovered because incapable of continued existence, thus :



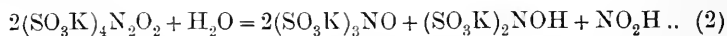
It is already known (Trans., 1889, 55, 765 ; 1894, 65, 539) that, in the presence of alkali, the nitroxy-radicles of a hydroxylaminesulphonate tend to separate from the sulphonate radicles. Such a tendency, exercised in the presence of undecomposed peroxyaminesulphonate, will lead to the production of hydroxylaminetrisulphonate and nitrite in the case of hydroperoxyaminesulphonate, and of the former salt and hypouitrite in the case of hydroxylaminedisulphonate, thus :



When the three equations are combined, the intermediate products disappear and the following equation is left,

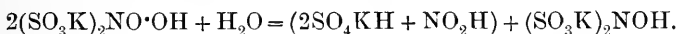


or, leaving the comparatively stable hydroxylaminedisulphonate unchanged,



It is fairly certain that the sulphate which, in greatly varying although never very large quantity, is always produced, does not come from the hydrolysis of the salt itself or from that of either the hydroxylaminetrisulphonate or hydroxylaminedisulphonate derived from it. For the trisulphonate is remarkably stable in the presence of alkali, and the disulphonate, although unstable in its presence,

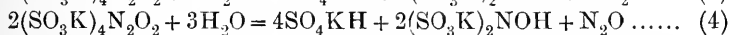
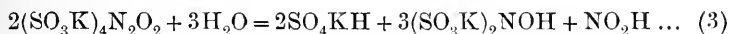
yields not sulphate but sulphite. As this is also true of hydroxylaminemonosulphonate, it may be assumed to be so in the case of peroxylaminesulphonate. The sulphate should therefore have another origin, which may well be taken to be the decomposition of the hydroperoxylaminesulphonate in circumstances in which it fails to interact with peroxylaminesulphonate, perhaps because the temperature of the solution is too low. In that case, it will naturally hydrolyse, one half becoming hydroxylaminedisulphonate by oxidising the other half into sulphate and nitrous acid,



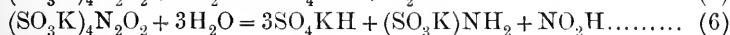
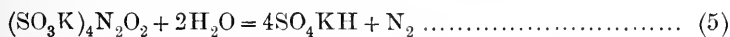
Or, it may well hydrolyse wholly into sulphate and nitrous oxide,



These equations combined with the primary equation give,



An equation to account for the production of nitrogen, and another for that of aminemonosulphonate are easily framed :



A justification of the lower of these equations and an illustration of the nature of the change expressed by it are to be found in the production of aminemonosulphonate from hydroxylaminedisulphonate when decomposing in presence of copper sulphate (Trans., 1900, 77, 978).

By combining these six equations in different ways, the various results obtained can be explained (p. 107), although the conditions for the occurrence of one mode of decomposition more than another are not yet ascertained.

*Sabatier's Bluish-violet Acid.*—Sabatier has studied the nature of the bluish-violet colour produced in a solution of nitrososulphuric acid (nitrosyl hydrogen sulphate) in the monohydrate of sulphuric acid by sulphur dioxide, and in other ways (p. 80), and has found this colour to be more closely like that of a solution of potassium sulphazilate than the colour of the latter is like that of a solution of potassium permanganate. On this ground and from a consideration of the circumstances which give rise to the colour, he has suggested that it is due to the presence in the solution of the acid of Fremy's salt, constituted according to the formula  $\text{ON}(\text{SO}_3\text{H})_2$ . Sabatier may be right, but there is much to be said against this opinion. Firstly, the tints of the two coloured solutions are not so similar as he asserts.

Secondly, certain striking contrasts may be observed in the chemical character of the two solutions. Potassium peroxyaminesulphonate is produced by the action of lead peroxide and is not attacked by it, whereas the coloured acid solution is at once oxidised by lead peroxide. Conversely, whilst this acid solution is indifferent towards sulphur dioxide and produced by it, potassium peroxyaminesulphonate is at once changed by this reagent.

Then, again, it has not proved to be possible either to convert potassium peroxyaminesulphonate into this violet acid solution or to effect the opposite change. Mr. S. Sekiguchi, a Post-graduate of this University, has kindly carried out some experiments in this direction. Making the mixtures very gradually and keeping them cold by ice and salt, he has poured the solution, prepared from nitrososulphuric acid and sulphur dioxide in sulphuric acid, into a solution of potassium hydroxide; and, on the other hand, an aqueous solution of potassium peroxyaminesulphonate into some concentrated sulphuric acid; in both cases, an almost immediate disappearance of the violet colour results. In the former case, too, the alkaline solution was evaporated and crystallised, without finding any of the hydroxylaminetrisulphonate which would result from the decomposition of peroxyaminesulphonic acid and might, to some extent, in accordance with its usual stability, escape decomposition.

#### *Details of Experiments.*

*The Exhaustive Action of Lead Peroxide on Hydroxylaminedisulphonates.*—Potassium  $2/3$ -normal hydroxylaminedisulphonate was boiled with excess of lead peroxide in about 15 times its weight of water, containing from  $1/5$  to  $2/5$  of a molecule of potassium hydroxide, until the solution had again become colourless. To the cold filtrate, just enough barium acetate was added to precipitate all sulphate present; the filtrate was then evaporated, and the hydroxylaminetrisulphonate crystallised out, as far as possible, and weighed. Potassium nitrite, produced in large quantity, was estimated in the mother liquor and alcoholic washings of the crystals of the hydroxylaminetrisulphonate by the urea method. Sulphate was found partly in solution and partly in the lead residue, which was extracted alternately with dilute nitric acid and potassium hydroxide. The sulphate, both in solution and residue, was estimated, and, in two cases, the soluble lead also, as a measure of the lead peroxide consumed.

In one experiment, 73.2 grams of salt gave 58.2 grams of trisulphonate in crystals, that is, 58.5 mol. of trisulphonate from 100 mol. of disulphonate, or 87.75 per cent. of the theoretical quantity. Nothing else was determined, and so high a yield of hydroxylaminetrisulph-

onate was only reached by adding alcohol to separate the last portions of the salt from the very concentrated nitrite mother liquor.

In another experiment, 125 grams of the disulphonate gave 97.33 grams of trisulphonate, equal to 57.33 mol. of trisulphonate to 100 mol. of disulphonate, or 86 per cent. of the calculated quantity. The amount of potassium sulphate was 21.5 mol. per 100 mol. of salt taken, which leaves sulphur for the trisulphonate equivalent to 59.5 mol., as against the 57.33 mol. of crystallised salt. Very much nitrite was found (37.5 mol. per 100 mol. of disulphonate taken), indicating the production of very little nitrous oxide. The only way to interpret this large production of nitrite is to assume that, whilst 89.25 per cent. of the salt was oxidised into trisulphonate and nitrite, and only 3 per cent. into sulphate and nitrous oxide, 7.75 per cent. was oxidised into sulphate and nitrite, an assumption which cannot be easily justified.

In an earlier experiment, in which the crystallisation of the trisulphonate was only imperfectly carried out, 136.33 grams of the disulphonate gave 84.33 grams of the crystalline product, that is, 100 mol. gave 45.56 mol., or 68.33 per cent. of the theoretical quantity. But since the quantity of sulphate, almost if not actually the only other sulphur compound produced, amounted to only 19 mol. per 100 of disulphonate, the actual yield of trisulphonate can have been little short of 60.33 mol. per 100. The nitrite, as determined by the urea method, was 28.4 mol. per 100 of disulphonate taken. But the lead peroxide consumed was in this case determined, and made out to be 71.5 mol. per 100 mol. of disulphonate, and this indicates the production of 31.8 mol. of nitrite. Accepting the mean of these numbers for the nitrite, it results that about 90 per cent. of the hydroxylamine-disulphonate was converted into trisulphonate and nitrite, and the rest into sulphate and nitrous oxide.

In an experiment with 35 grams of potassium hydroxylaminedisulphonate, in which the crystals of hydroxylaminetrisulphonate were not weighed, 100 mol. yielded 13 mol. of sulphate and 26 mol. of nitrite. Calculating from these quantities, 78 per cent. of the salt was oxidised into trisulphonate and nitrite, 15.5 into trisulphonate and nitrous oxide, and 6.5 into sulphate and nitrous oxide. The trisulphonate produced will therefore have been about 93.5 per cent. of the calculated quantity, or 62.33 mol. per 100 mol. of disulphonate.

Another experiment was made on the normal sodium hydroxylaminedisulphonate (*Trans.*, 1894, 65, 546) in dilute solution, 11.33 grams being taken without any addition of sodium hydroxide, because the alkalinity of the salt was sufficient to protect it. But in this experiment, only the quantities of lead peroxide consumed and of sulphate formed were estimated. Exactly as happened in the experi-

ment with the potassium salt, 71.5 mol. of lead peroxide were consumed per 100 mol. of sodium salt. The sulphate amounted to 34 mol. per 100 mol. of salt used, more, that is, than in the experiments with the potassium salt. The calculated quantity of sodium hydroxylamine-trisulphonate was correspondingly lower, 55 mol. per 100 mol. or 82.75 per cent. of the theoretically possible quantity.

*Reduction of Potassium Hydroxylaminetrisulphonate by Sodium Amalgam.*—In the interaction between sodium amalgam and potassium hydroxylaminetrisulphonate in aqueous solution, the two liquids become warm, and the action is soon over if the two are well shaken together. No gas is evolved, and nothing is left in solution but the two salts, sulphate and aminedisulphonate (iminosulphate). The latter is easily recognisable by its separating as the very sparingly soluble  $2/3$ -normal potassium salt when the solution is nearly neutralised with an acid, and also by its nearly insoluble normal mercury-potassium salt (Trans. 1892, 61, 976; 1896, 69, 1629). But the salt was also analysed quantitatively (p. 97) in order to demonstrate its nature beyond question. By cautiously adding hydrochloric acid to the cold solution until it has become almost neutral to methyl-orange, and then precipitating with barium chloride, the sulphate is partially separated from the aminedisulphonate; the latter may then be estimated as sulphate in the filtrate after hydrolysis at  $150^{\circ}$ . In an experiment carried out in this way on 2.447 grams of potassium hydroxylamine-trisulphonate, the barium sulphate precipitate was washed with cold, and then with hot, water, ignited, and weighed. The sulphate from the hydrolysed aminedisulphonate was treated as in an ordinary sulphate determination. In this way determined, 34.79 per cent. of the sulphur came out as sulphate and 64.88 per cent. as aminedisulphonate, leaving 0.33 per cent. unaccounted for. In accordance with the equation, the actual numbers should have been 33.33 and 66.67 per cent. respectively. By other experiments, it was, however, established that some of the aminedisulphonate was precipitated with the sulphate. No doubt, also, some barium chloride was carried down.

Potassium hydroxylaminetrisulphonate, 1.441 grams, was reduced by sodium amalgam, and the solution neutralised and precipitated in the cold by barium chloride as above described. The washed precipitate was then heated for 4 hours at  $150^{\circ}$  with dilute hydrochloric acid in a sealed tube. The acid was nearly neutralised, and the barium sulphate collected, washed, and weighed as usual. The filtrate from this yielded a fresh precipitate with barium chloride, for the barium aminedisulphonate, which was precipitated with the sulphate, had been hydrolysed into barium sulphate and ammonium hydrogen sulphate. Therefore, from the weight of the main precipitate of sulphate was deducted that of the small quantity last

obtained, and the remainder taken as sulphate actually produced by the sodium reduction. It amounted to the equivalent of 34.20 per cent. of the total sulphur. The aminedisulphonate in the original filtrate from crude sulphate was determined by hydrolysing and weighing its sulphur as sulphate. To the weight of this was added twice that of the barium sulphate obtained, as just described, from the soluble sulphate extracted by hydrolysing the crude barium sulphate, because twice that quantity represented the total sulphur of the aminedisulphonate precipitated along with the actual sulphate. This sum was equivalent to 65.75 per cent. of the total sulphur. That these data still deviate from the calculated numbers is no doubt due to the adhesion of a little barium chloride to the sulphate when precipitated in the cold. The barium of this chloride will have rendered insoluble some of the sulphate which should have dissolved out through the hydrolysis of the aminedisulphonate simultaneously precipitated. There seems, therefore, to be no reason for doubting the quantitative accuracy of the equation given on p. 82.

An experiment was then tried to see whether closer results could not be got by removing as much as possible of the aminedisulphonate from the solution before precipitating the sulphate, first crystallising out most of it from the nearly neutralised solution, and then removing some of the remainder as the mercury-potassium salt, by digesting the solution with mercuric oxide. This method, however, did not give better results than the preceding.

*Reduction of Potassium Hydroxylaminetrisulphonate by the Zinc-copper Couple.*—The reduction of the trisulphonate was successfully effected by boiling its solution (to which a few drops of sodium acetate solution had been added in order to protect the salt from hydrolysis) with some zinc-copper couple. But in consequence of the necessity of boiling the solution, hydrolysis of the aminedisulphonate is apt to set in.

Some aminedisulphonate prepared by the sodium amalgam method, and another sample, prepared by the zinc-copper couple, were analysed with the following results:

	By sodium.	By zinc-copper.	Calc.
Potassium.....	30.68	30.72 —	30.89
Sulphur.....	25.09	24.85 25.94	25.30
Nitrogen .....	5.32	6.16	5.54

*Hydrolysis of a Hydroxylaminetrisulphonate.*—The complete hydrolysis of the hydroxylaminetrisulphonates is more difficult to effect than that of any other of Fremy's salts. In the quantitative analysis of the salts, it was found necessary to keep the acidified solution for 5 hours at 180—200°. In the case of the potassium salt, the mean

percentage of sulphur then came out as 23.18; at 150° only, for 4 hours, it was 22.85; and at 90—100° for 5 hours, and then 3 hours at 130°, it gave only 22.64. In this case, the nitrogen of the hydroxylamine obtained (as measured by the iodine method) amounted only to 2.5 per cent. In another case, where the hydrolysis was allowed to go on for 48 hours at 90—95°, and then 2 hours at 130—134°, the nitrogen obtained as hydroxylamine was 2.71 per cent. (79.75 per cent. of total nitrogen).

*Inactivity of Sulphites towards Hydroxylaminetrisulphonates.*—Potassium hydroxylaminetrisulphonate weighing 2 grams, in sufficient water to keep the salt in solution, was left for 3 days with 3 grams of potassium metasulphite, rendered slightly alkaline to lacmoid paper (whilst strongly acid to litmus). The sulphite was then precipitated by barium hydroxide and the filtrate evaporated. In this way 1.98 grams of the hydroxylaminetrisulphonate crystallised out. The analysis of the salt thus recovered is given as that of II among the analyses of the salt below.

*Analysis of Potassium Hydroxylaminetrisulphonate.*—Although this has been analysed by previous workers, it was necessary to make several careful and full analyses in order to establish the fact that it contains more water of crystallisation than the proportion stated by Claus and by Raschig. Four separate preparations were analysed.

I. 0.4954 substance gave 0.3117 potassium sulphate; 0.5088 gave 0.8581 barium sulphate; 0.3387 gave 0.5680 barium sulphate; 0.2821 substance, finely powdered and heated in a current of dried air, first at 95° and then up to 110°, lost 0.0138; 0.2174 lost in this way 0.0101.

II. 0.2272 substance gave 0.1429 potassium sulphate; 1.0676 treated with sodium amalgam for 24 hours and then hydrolysed at 150° for 3 hours, gave 1.7918 barium sulphate and ammonia = 25.59 c.c. *N*/10 acid.

III. 0.2288 substance gave 0.1451 potassium sulphate; 0.1003 gave 0.1710 barium sulphate.

IV. 0.8505 substance gave 0.5347 potassium sulphate; 0.34475 gave 0.5799 barium sulphate; 2.4425, by sodium amalgam treatment and hydrolysis at 150° for 3 hours, gave ammonia = 51.38 c.c. *N*/10 acid; 0.7650, by the Dumas method, gave 22.3 c.c. moist nitrogen at 16° and 758 mm.

	Potassium.	Sulphur.	Nitrogen.	Water.
Found, I ... ..	28·25	{ 23·18 23·05	— —	(4·89) (4·65)
„ II .....	28·24	23·07	3·37	—
„ III .....	28·47	23·42	—	—
„ IV .....	28·23	23·12	{ (2·95) 3·39	— —
Mean .....	28·30	23·18	3·38	(4·77)
Calculated for $1/1\text{H}_2\text{O}$ .....	28·95	23·71	3·46	4·49
„ $3/2\text{H}_2\text{O}$ .....	28·32	23·19	3·39	6·52
Fremy .....	28·02	23·40	3·48	—
Claus, found (taking old atomic weights)	28·63	—	3·24	5·04
„ „ „	28·55	—	—	5·20
„ „ „	28·67	23·69	—	5·01
„ „ „	28·79	23·76	3·31	4·71
Claus, mean .....	28·66	23·73	3·28	4·99
„ calc. (taking old atomic weights)	28·88	23·70	3·45	4·44
Raschig .....	28·47	23·64	—	—
„ .....	28·54	23·38	—	—

Claus has also given the results of five closely concordant analyses of the anhydrous salt, and should therefore have experienced no difficulty in rendering it anhydrous. In the attempts to determine total water, recorded above, the residue was always acid in consequence of the unavoidable hydrolysis and fixation of some of the water of crystallisation. A discussion of this matter is given on page 83.

*Analysis of the Sodium Salt.*—Two distinct preparations of the sodium salt were analysed :

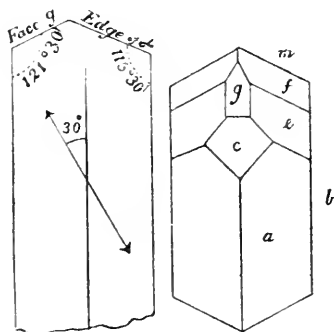
I. 0·4910 substance gave 0·2801 sodium sulphate ; 0·3845 gave 0·7174 barium sulphate, after hydrolysis at  $200^\circ$  for 3 hours. Hydrolysed at only  $160^\circ$  for 5 hours, 0·4548 gave 0·8378 barium sulphate, = sulphur 25·30 per cent. only.

II. 0·6097 substance gave 0·3455 sodium sulphate ; 0·1750 gave 0·3268 barium sulphate, after hydrolysis at  $210^\circ$  for 3 hours ; 0·7533 gave 24·0 c.c. moist nitrogen at 760·8 mm. and  $17^\circ$ , = 0·027 nitrogen.

	Sodium.	Sulphur.	Nitrogen.
Found, I .....	18·50	25·64	—
„ II .....	18·36	25·67	3·70
$\text{Na}_3\text{S}_3\text{NO}_{10}, 2\text{H}_2\text{O}$ .....	18·42	25·62	3·76

*Crystallography of Sodium Hydroxylaminetrisulphonate.*—Professor Jinbo has kindly given me the following description of the crystals of this salt, which were examined under his directions by Mr. M. Yōtsuki, University Post-graduate. Thick, tabular, monoclinic crystals, about 3 mm. long and 2 mm. wide, elongated in the direction of the vertical axis. The observed faces are of seven kinds, of which *b* is the largest

and apparently the plane of symmetry.  $m$ , making with  $b$  an angle of about  $115^\circ$ , may be taken as a prism;  $d$ ,  $e$ , and  $f$  as pyramids;  $c$  as the base, and  $g$  as a positive orthodome. Two other faces in the zone



of the orthodiagonal are sometimes observed. A crystal laid flat on the clinopinacoid shows an extinction angle of  $30^\circ$  to the vertical axis, in the acute angle between this and the clinodiagonal.

*Analysis of the Ammonium Salt.*—The total nitrogen of the ammonium salt was determined by the Dumas method.

	Found.	$2\text{H}_{12}\text{O}_{10}\text{N}_4\text{S}_3 \cdot 3\text{H}_2\text{O}$	$\text{H}_{12}\text{O}_{10}\text{N}_4\text{S}_3 \cdot \text{H}_2\text{O}$
Sulphur .....	27.63	27.36	28.08
Nitrogen .....	16.06	15.98	16.40

*Analysis of the Basic Lead Salt.*—The salt was dried for analysis in a current of dry air at  $100^\circ$  in the case of preparation I, and at  $110^\circ$  in that of II. The salt was quite free from potassium but contained a trace of acetate.

	Found.	Found.	$\text{H}_9\text{O}_{19}\text{NS}_3\text{Pb}_6$
Lead .....	74.41	74.14	74.71
Sulphur .....	5.99	—	5.79

*Determination of the Molecular Magnitude of Sodium Hydroxylaminetrisulphonate.*—This was carried out by Löwenherz's method with melted sodium sulphate crystals (*Zeit. physikal. Chem.*, 1896, 18, 70).

Hydrated salt.	Anhydrous salt.	Fused sodium sulphate.	$\Delta t.$	M.W.
2.479	= 2.2411	59.411	$-0.369^\circ$	332.20
3.478	= 3.0210	57.520	$-0.510$	335.56

$\text{O}_{10}\text{N}_3\text{S}_3\text{Na}_3$  requires 339.37

*Molecular Magnitude of Normal Sodium Hydroxylaminedisulphonate.*—

Crystallised salt.	Fused sodium sulphate.	$\Delta t.$	M.W.
1.220	36.8180	- 0.39°	233
2.023	37.1980	- 0.74	239.6
$O_7NS_2Na_3$ requires 239.3			

With this molecular weight the nitrogen is necessarily trivalent.

*Solubility of Peroxylaminesulphonate in N/10 Solution of Potassium Hydroxide.*—The purified salt, previously washed on the porous tile with some of the solvent, was shaken with it for from 15 to 20 minutes, the temperature of the solution being 29°. After some time, 5 c.c. of the clear solution were withdrawn with a pipette. The rest of the solution, along with the undissolved salt, was left for some hours in ice, when again 5 c.c. were taken out, the temperature being 3°. The two portions were each weighed and the amount of dissolved salt ascertained by a sulphur determination. It was thus found that 0.163 gram of salt was dissolved in 5.03 grams of its alkaline solution at 29°, and that 0.027 gram was dissolved in 4.980 grams of its solution at 3°.

*Interaction of Potassium Peroxylaminesulphonate and Normal Potassium Sulphite.*—To a solution of 3.6 grams of potassium peroxylaminesulphonate, containing only a very small quantity of potassium hydroxide, a solution of normal potassium sulphite (neutral to phenolphthalein) was added from a burette, with constant stirring, until the violet colour of the solution was entirely discharged. The change took place quickly but not instantly. The quantity of sulphite required was only a little more than that indicated by theory. After a short interval, baryta water was added to precipitate the excess of sulphite and the hydroxylaminedisulphonate. The excess of baryta was removed from the filtered solution by carbon dioxide and the filtered solution evaporated so as to get out as much as possible of the sparingly soluble potassium hydroxylaminetrisulphonate. Some more of this salt was precipitated by adding twice the volume of alcohol and leaving the mixture for some time. The total trisulphonate thus separated weighed 2.268 grams, or 81.5 per cent. of the calculated quantity.

The barium precipitate was triturated in a mortar with very dilute acetic acid, added very slowly so as to avoid as far as possible having any local excess of acid. When the solution had become neutral to phenolphthalein, the undissolved barium sulphite was filtered off. Potassium carbonate in slight excess was added and the whole left for a day. Then, the solution, filtered from the barium carbonate and neutralised with acetic acid, was concentrated in a vacuum over sulphuric acid and mixed with twice its volume of alcohol. In 12 hours, the quantity of precipitated crystalline 2/3-normal hydroxylamine-disulphonate weighed 1.55 grams, this being equal to 76 per cent. of the

calculated quantity. It was pure, except for a trace of aminetrisulphonate (nitrilosulphate), doubtless due to the action of the sulphurous acid unavoidably liberated in the process of separating the barium sulphite from its own barium salt by acetic acid. It was identified by hydrolysis into sulphate and hydroxylaminemonosulphonate, and above all by its producing the bluish-violet peroxyamine-sulphonate when warmed with lead peroxide and a small amount of alkali. No nitrite was found in the mother liquor of the hydroxylaminetrisulphonate, showing that the production of the latter salt had not been due to spontaneous decomposition of the peroxylaminesulphonate. Hydroxylaminetrisulphonate and disulphonate are, in fact, the only substances which could be detected among the products of the interaction of the peroxylaminesulphonate and sulphite. Since, therefore, the separated quantities of these products were found to be in approximately molecular proportions, and as these salts are not insoluble, even in their alcoholic mother liquors, it may be regarded as proved that the interaction which takes place is exclusively that represented by the equation on p. 90.

*Spontaneous Decomposition of Potassium Peroxylaminesulphonate.*—The principal products of the spontaneous decomposition of a peroxyaminedisulphonate in hot alkaline solution are easy to recognise. Unless very dilute, the solution yields crystals on cooling and more on evaporation. At first the sparingly soluble hydroxylaminetrisulphonate alone crystallises, and later on both this and the equally sparingly soluble hydroxylaminedisulphonate. In each case the crystals are characteristic and easily distinguished. The presence of the disulphonate in the solution is quickly and distinctively indicated, as has just been mentioned, by warming with a small quantity of lead peroxide, which gives it again the bluish-violet colour of peroxyamine-sulphonate. By removing sulphate and hydroxylaminedisulphonate from the solution by barium hydroxide, nearly all the hydroxylaminetrisulphonate can be crystallised out; the mother liquor containing the nitrite may then be tested in any of the usual ways for this salt.

It was important to know whether any nitrate is formed by the decomposition, and therefore necessary first to get rid of all the nitrite present by a process that does not convert any of it into nitrate. The nitrite was accordingly changed into aminetrisulphonate (nitrilosulphate) by adding enough potassium carbonate and then passing in sulphur dioxide until the solution became acid, at which point the aminetrisulphonate that had been produced at once hydrolysed (Trans., 1892, 61, 954). Lastly, by blowing in air until all the remaining sulphur dioxide had been expelled, the acid solution was left free from either nitrite or sulphite, and, therefore, ready for testing for nitrate. None of this salt was found. The application of the

process of sulphonating the nitrite to the determination of total nitrogen in solution, is described on p. 104.

The testing for aminemonosulphonate (aminosulphate) among the products of decomposition of a peroxyaminesulphonate is not an easy matter. The method adopted was to oxidise all the hydroxylaminedisulphonate by boiling the solution with lead peroxide until it was again colourless. The nitrite was then oxidised by pouring the solution into potassium permanganate solution to which sulphuric acid had been added. Mercuric nitrate solution then precipitated from it a little oxymereuric aminemonosulphonate (*Trans.*, 1896, 69, 1649), which, when treated with hydrogen sulphide, left the acid again in solution. By evaporation and addition of strong sulphuric acid, the acid was obtained in characteristic crystals (*loc. cit.*, 1642), which were sometimes weighed.

The quantitative examination of the solution is a troublesome and less satisfactory operation. The peroxyaminesulphonate can hardly be obtained for weighing in the dry and pure state, because of its instability. Therefore, after its composition had been found, from concordant analyses of four different preparations, to be that ascertained by previous workers, the preparation of the solution and its analysis after the salt had all decomposed were carried out in the following way. The peroxyaminesulphonate, recrystallised two or three times from hot water made alkaline with potassium hydroxide, was drained for a short time on a tile from its mother liquor, and at once dissolved in suitable quantity in water to which had been added a measured quantity of potassium hydroxide. The solution was maintained at the boiling temperature until colourless through the complete decomposition of the salt. The cold solution was then weighed off into four portions: one of 5 per cent. of the whole, for estimating the amount of peroxyaminesulphonate that had been dissolved; another of 15 per cent., for estimating the quantity of hydroxylaminetrisulphonate produced; a third and a fourth portion, each of 40 per cent., for estimating in one the quantity of sulphate, and in the other that of nitrite produced. The quantity of peroxyaminesulphonate taken was determined by weighing as barium sulphate the total sulphur in the solution. To ensure the hydrolysis of all the sulphonate, the solution was heated with hydrochloric acid in sealed tubes for 4—5 hours at 180—200°.

To determine the quantity of sulphate which had been produced, very dilute hydrochloric acid was added with constant stirring until the solution was only barely alkaline to phenolphthalein, then much ammonium chloride was added before precipitating with barium chloride, in order to keep the hydroxylaminedisulphonate in solution as far as possible. The impure sulphate, washed with ammonium

chloride solution on the filter, was transferred to a beaker, and digested in the cold with very dilute hydrochloric acid, washed again on the filter with boiling water, and then ignited in the usual way.

The hydroxylaminetrisulphonate was estimated by leaving the solution with sodium amalgam for two days, occasionally shaking the two together so as to convert this salt into hydroxylaminedisulphonate, and then all the hydroxylaminedisulphonate in the solution into aminedisulphonate (iminosulphate). The mercury having been filtered off and washed, hydrochloric acid was added to the solution until it was only just alkaline to methyl-orange, and then an excess of ammonium chloride was introduced. The sulphate was finally precipitated and treated as before described. Deducting from this quantity of sulphate that which was present before the treatment with sodium amalgam, there remained the sulphate equivalent to one-third of the sulphur of the hydroxylaminetrisulphonate, from which the quantity of this salt was calculated. Assuming hydroxylaminedisulphonate to be the only other sulphur compound produced in the decomposition of the peroxyaminesulphonate—an assumption which is nearly exact—the amount of this salt was then calculated as being equivalent to the sulphur not found either as sulphate or hydroxylaminetrisulphonate. The slight error in this assumption is caused by the production of very small quantities of aminemonosulphonate (aminosulphate). As to the last-named salt, it has not been possible to do more than ascertain that its quantity is usually quite small, although 2 mol. of the crystalline acid (p. 103) per 100 mol. of hydroxylaminedisulphonate oxidised by the lead peroxide were once actually obtained. In other words, the amount of sulphur found as aminemonosulphonate was in this instance 1.03 per cent. of that of the hydroxylaminedisulphonate used.

To determine the total nitrogen in the solution, the nitrite was completely sulphonated to aminetrisulphonate (nitrilosulphate) by adding enough potassium carbonate for the purpose and then passing in sulphur dioxide until a piece of lacmoid-paper was just reddened (Trans., 1892, 61, 954). Next, the hydroxylaminetrisulphonate in the solution was reduced by sodium amalgam, as above described, to sulphate and aminedisulphonate. Having thus brought all the nitrogen into aminesulphonates, the hydrolysis of these substances by hydrochloric acid was effected by heating, first, on the water-bath until all the sulphur dioxide had been expelled, and then for some hours in a pressure-tube at 150°. The solution distilled with alkali gave up all its nitrogen as ammonia. The difference between this and that originally present as peroxyaminesulphonate gives, indirectly, the quantity of nitrogen in the gases, whilst the difference, again, between the total nitrogen in the solution

and the sum of the quantities found as disulphonate and trisulphonate is the nitrogen which was present as nitrite.

Although the experimental work in estimating sulphate and hydroxylaminetrisulphonate was performed with great care, no high degree of accuracy in the results could be expected. A test experiment was made to see to what extent the method was imperfect. A solution was prepared by dissolving potassium sulphate, potassium hydroxylaminetrisulphonate, potassium hydroxylaminedisulphonate, and sodium nitrite in water to every 100 c.c. of which 5 c.c. of *N*/10 solution of potassium hydroxide had been added. The solution was twice analysed for sulphate and trisulphonate in the way described above. The quantities, taken and found, are here given in grams per 100 c.c.

	Taken.	Found.	
Trisulphonate.....	2.580	2.547	2.624
Sulphate .....	0.347	0.380	0.373
Disulphonate .....	0.622	0.629	0.551
Nitrite .....	0.208	0.212	0.217

From this experiment, it seems that the sulphate may come out nearly 10 per cent. too high, no doubt for two reasons; one that being precipitated in the cold, the barium sulphate retained other salts with it; the other and principal reason being that, in the process of neutralising the solution, some of the disulphonate must be decomposed, yielding sulphate. The numbers for the trisulphonate are much more satisfactory, being less than 1.7 per cent. too high, apparently because they represent the difference between two sulphate determinations, the error in the one counterbalancing the corresponding error in the other. When, however, we come to the numbers for the disulphonate, which are calculated from those for the other substances, it is seen how large the error may become, being in one case as much as 11.4 per cent. too low. Similarly, the quantity of nitrite, calculated from those of the other substances, may come out as much as 4.5 per cent. too high. The expression of the errors as percentages only holds good, of course, where the salts in an actual experiment are nearly in the same proportions as here taken, as they were generally found to be.

The quantities of nitrite and of gases yielded by the peroxyamine-sulphonate may also be each determined directly. The nitrite may be estimated by the urea method, as stated on p. 94, most of the sulphonate salts having first been crystallised out and washed with alcohol. The method for collecting and measuring the gases produced during the decomposition consists in letting this proceed in a closed vessel from which the air is withdrawn. A stout-walled, cylindrical bolt-head, of about 250 c.c. capacity, with a stopcock sealed on to it, was exhausted

and then opened with its mouth in the solution of peroxyamine-sulphonate and potassium hydroxide. About 200 c.c. were allowed to enter, holding between 6 and 7 grams of the salt in solution. The tube was again exhausted and the stopcock being then closed, the salt was decomposed by heating the solution. When cold, the apparatus was connected with a Sprengel pump and the gases drawn off and measured. They proved to be free from nitric oxide, but, on treatment with strong alcohol, a small proportion of nitrogen remained undissolved. The experiments on this method of determining the gases have been very few, and not such as have admitted of their utilisation in this paper, beyond giving proof that nitrogen in small quantity is generated along with the nitrous oxide, which is the main constituent of the gaseous mixture, and that the quantity of the gases may vary greatly in different experiments.

Where the decomposition of the peroxyaminesulphonate proceeds in the presence of lead peroxide, as it is made to do in the preparation of hydroxylaminetrisulphonate, no hydroxylaminedisulphonate can remain in the solution, and in place of it is found principally an increase in the quantities of trisulphonate and nitrite. The absence of the disulphonate simplifies the analysis, as is seen on p. 94.

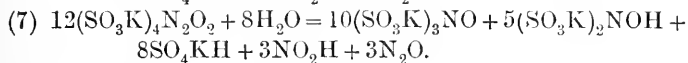
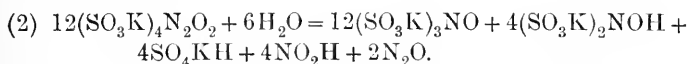
Eight analyses of the products of the spontaneous decomposition of the peroxyaminesulphonate were made. In Expt. 1, a solution holding 2.3184 grams of potassium peroxyaminesulphonate and 60 c.c. of *N*/10 solution of potassium hydroxide was made up to 150 c.c. and then found to weigh 150.79 grams. It was slowly heated to the boiling point, and kept boiling till decolorised. Expt. 2.—The solution, weighing 234.3 grams and containing 2.547 grams of the salt and 72.3 c.c. of *N*/10 potassium hydroxide, was left in the cold for two days, and then boiled until colourless. During the boiling, a reflux condenser was used to retain the water in the solution. Expt. 3.—A solution, weighing 120.42 grams and measuring 120 c.c. of 1.22 grams of salt and 11.4 c.c. of *N*/10 potassium hydroxide, was decomposed by boiling. Expt. 4.—The solution weighed 134.9 grams, and contained 1.8576 grams of salt and 30 c.c. of *N*/10 potassium hydroxide; it was decomposed by boiling. Expt. 5.—A solution of 0.6601 gram of salt and 20 c.c. of *N*/10 potassium hydroxide, weighing 34.25 grams, was left in the cold for a week, when it had become colourless. Expt. 6.—Like the last, but the solution weighed 266.7 grams and the salt 5.27 grams, whilst the potassium hydroxide was taken in about the same proportion as before. Expt. 7.—The solution was a portion of the same as had been used for Expt. 2. When kept in a closely-stoppered flask, it had only lost all its colour after about five months. Expt. 8.—This experiment differed from the others in the use of baryta-water in place of potassium hydroxide, and to this must be

attributed the production of so much sulphate and hydroxylamine-disulphonate. The solution took a month to lose all its colour.

In the table, the numbers of molecules of the several products yielded by  $100(\text{SO}_3\text{K})_4\text{N}_2\text{O}_2$  are given according to calculation from the analyses made in the way above described, and without any corrections for the probable, but variable, errors inherent in the method.

Mol. weight.	1.	2.	3.	4.	5.	6.	7.	8.
$(\text{SO}_3\text{K})_3\text{NO}$ .....	85	102.3	101.7	77.7	91.4	85.3	86	12.9
$(\text{SO}_3\text{K})_2\text{NOH}$ .....	61	30	23.6	65.4	42.3	42	40.4	133.2
$\text{SO}_4\text{KH}$ .....	23	33	47.6	36	41.2	60	61.2	94.7
$\text{HNO}_2$ .....	49	26	32.5	50.2	35	37	26.4	—

Without further experiments, it does not seem possible to account for the wide variations in these numbers, except where baryta was used. From Expts. 2 and 7, started on portions of the same solution, it seems clear that, with the slow decomposition of the peroxyaminesulphonate which goes on in the cold, instead of the rapid change which occurs at a boiling heat, molecular quantities of hydroxylaminedisulphonate and sulphate take the place of some of the hydroxylaminetrisulphonate, and that a little of the hydroxylamine-disulphonate is replaced by its equivalent of sulphate and nitrous oxide. This becomes more obvious when equations in these two cases are given with only 12 molecules instead of 100 molecules of decomposing peroxyaminesulphonate. This is possible without deviating from the numbers found more than the imperfections of the analytical method allow.



The production of small quantities of nitrogen and aminemonosulphonate is of necessity ignored in the above calculations.

The author gratefully acknowledges his indebtedness to Dr. Divers, F.R.S., for a thorough revision of his manuscript.

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XI.—*Peroxyaminesulphonic Acid.*

By EDWARD DIVERS.

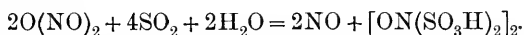
ALTHOUGH unrecorded in works on chemistry or chemical technology, it has long been known to inspectors and workers of the lead-chamber process for manufacturing sulphuric acid, that when, through improper working of the chambers, sulphur dioxide is allowed to pass into the Gay-Lussac tower, it produces with the nitrososulphuric acid, also present in the tower, what is called "purple acid," together with an effervescence due to the escape of nitric oxide (Carpenter and Linder, *J. Soc. Chem. Ind.*, 1902, 21, 1492). Sabatier has shown (*Compt. rend.*, 1896, 122, 1417, 1479, and 1537; 123, 255) how to give an intensely bluish-violet colour, evidently the same as that of "purple acid," to the monohydrate of sulphuric acid holding nitroso-sulphuric acid in solution, either by passing sulphur dioxide into it, or by mixing it with sulphuric acid of similar strength containing dissolved sulphur dioxide. Such a sulphuric acid solution of sulphur dioxide may also be treated for some time with a current of nitric oxide and air; or, excluding air, the nitric oxide alone will produce the colour, when a very small quantity of either copper sulphate or ferric or ferrous sulphate has been previously dissolved in the acid. Lastly, certain metals and other substances serve to produce this colour, or a modification of it, by acting on nitrososulphuric acid in monohydrated sulphuric acid, among them being finely divided copper, silver, or mercury. Sabatier has not isolated the substance which gives this violet colour to sulphuric acid treated by the foregoing processes, but has suggested that it may be the unknown acid of Fremy's *sulphazilate*, which he renames *nitrosodisulphonic acid*.

Now, in the preceding paper on peroxyaminesulphonates, Haga has adduced reasons for doubting the correctness of Sabatier's suggestion that the bluish-violet acid is sulphazilic acid, that is, peroxyamine-sulphonic acid. There is also one consideration which, although not mentioned by Haga, may, nevertheless, have affected his judgment. This is the fact that a substance which, according to Haga's most conclusive evidence, must be a peroxide, should be produced in the ways described by Sabatier. But this difficulty and those raised by Haga all seem to disappear when the changes which give rise to the acid and the very different conditions for the production of the salt and of the acid are all more closely examined, and leave nothing in the way of accepting the view that this acid is peroxyaminesulphonic acid.

The fact that the violet acid is dissolved in sulphuric acid, whereas the violet salt is in aqueous solution, has to be taken into account

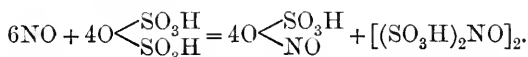
when the differences in the behaviour of the two are under consideration. It will then be seen that these differences are really not greater than those between a sulphuric acid solution of nitrous acid (as nitroso-sulphuric acid) and an aqueous solution of potassium nitrite. The latter when acidified and the former when diluted both quickly lose most of the nitrous acid, there being no stable existence of this acid in the intermediate conditions. Potassium nitrite solution is unaffected by hydrogen peroxide or potassium permanganate, being, in fact, producible from nitric oxide by alkaline hydrogen peroxide (Carpenter and Linder, *loc. cit.*), and from hyponitrite by permanganate (Thum, *Monatsh.*, 1893, 14, 294), whereas nitrous acid is converted by these reagents into nitric acid. Lead peroxide may therefore very well be active towards a sulphuric acid solution of peroxyamine-sulphonic acid, although it does not interact with an aqueous solution of its salts. Again, that sulphur dioxide should not interact with peroxyaminesulphonic acid in presence of much sulphuric acid, and yet be very active towards a salt of the acid in water, may well be an instance of what indeed happens in the case of mercuric oxy-salts, on which, in presence of much sulphuric acid, sulphur dioxide is no longer active (Trans., 1886, 49, 576), or in that of ferric salts, which are very much more easily reduced by sulphur dioxide in the absence of sulphuric acid than in the presence of excess of it. Similarly, it may further be properly maintained that it does not follow that hydroxylaminetrisulphonic acid should be produced from peroxyamine-sulphonic acid in sulphuric acid solution because its salt is produced in a neutral or an alkaline aqueous solution of a peroxyamine-sulphonate. This contention being admitted, the non-formation of this acid, observed by Haga, is not significant.

Since the well-known compound, nitrososulphuric acid, is not a sulphonic derivative, as Sabatier takes it to be, but the mixed anhydride of nitrous and sulphuric acids, the nature of its conversion into the violet acid is easy to understand. Regarding the mixed anhydride as being simply nitrous anhydride (the sulphuric acid being undecomposed), the production from it of nitric oxide and peroxyaminesulphonic acid is seen to be only its usual decomposition into nitric oxide and nitric peroxide, except that the latter product is now sulphonated :

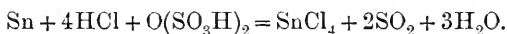


When metallic copper is used in place of sulphur dioxide, the generation of the necessary sulphur dioxide by the action of the metal on the pyrosulphuric acid of the nitrososulphuric acid only introduces an interesting complication. Pyrosulphuric acid at once interacts with copper in the cold (Trans., 1885, 47, 638).

There remains to be considered the production of the purple acid along with nitrososulphuric acid from nitric oxide and sulphuric acid in the presence of cupric or ferric sulphate as a catalytic agent. The sulphuric acid being represented as existing in its pyro-state (the form in which it acts in presence of an oxide of nitrogen), the change is expressed by the equation:



As to the peroxidising action of pyrosulphuric acid here shown, it may be well to recall the action of the acid on metallic tin in presence of hydrochloric acid (Heumann and Koechlin, *Ber.*, 1882, 15, 420):



In this equation the stannic chloride and the sulphur dioxide together take the place of the peroxyaminesulphonic acid in the previous one, for  $[\text{ON}(\text{SO}_3\text{H})_2]_2$  can evidently be expanded into  $\text{N}_2\text{O}_4 + 4\text{SO}_2 + 2\text{OH}_2$ .

It is difficult to conceive of any other rational interpretations of Sabatier's remarkable results than those given above, and these are all consistent with the assumption that the purple acid is not merely isomeric, but actually identical with peroxyaminesulphonic acid, and is therefore a peroximide and an exclusively trivalent nitrogen compound.

## XII.—*Constitution of Nitric Peroxide.*

By EDWARD DIVERS.

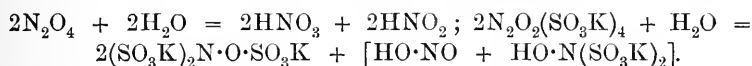
IN a paper now appearing (this vol., p. 78), Haga has demonstrated that Fremy's *sulphazilate* is an oxime-peroxide and a trivalent nitrogen compound. If Hantzsch and Semple's suggestion is accepted (*Ber.*, 1895, 28, 2744; compare Piloty and Schwerin, *Ber.*, 1901, 34, 1884 and 2354), that Fremy's salt is also a sulphonated nitric peroxide, it follows that the constitution of nitric peroxide is at last determined, being that of *nitrosyl peroxide*. Hantzsch and Semple must be right, for, after Haga's researches, a sulphazilate as a peroxyaminesulphonate cannot be supposed to be other than a sulphonated nitric peroxide. It only remains, therefore, to show that nitric peroxide is a true peroxide in its chemical relations.

It is formed from nitric oxide and oxygen, just as sodium peroxide is formed from sodium and oxygen. Nitrous acid cannot, indeed, be shown to pass simply into it and back again, as a hydroxylamine-

disulphonate (sulphonated nitrous acid) changes into a peroxyamine-sulphonate, but that is only on account of its own instability and that of nitrous acid.

Its interaction with organic oximes, in which it converts these substances into peroxides and becomes hydrogenised into nitrous acid (Scholl), is in accordance with its nature as a true peroxide. Similarly, it converts a hydroxylaminedisulphonate into a peroxyaminesulphonate (Haga).

Nitrosyl peroxide and a peroxyaminesulphonate both interact with water in essentially the same way, the apparent difference being due to the limits imposed by the sulphonation in the case of the latter substance. The former yields half its nitrogen as nitric acid and half as nitrous acid, whilst the latter yields half its nitrogen as a mixed anhydrosulphate (hydroxylaminetrisulphonate) and the other half as nitrous acid and sulphonated nitrous acid (hydroxylaminedisulphonate):



It would seem, therefore, that, wholly on the evidence afforded by Haga's work, it can now be confidently asserted that dinitric peroxide is nitrosyl peroxide and a compound of exclusively trivalent nitrogen. The constitution of mono-nitric peroxide, in regard to these two points, remains to be considered, but can hardly be very different.

Hantzsch and Semple have suggested (*loc. cit.*) that the bluish-violet dissolved form of a peroxyaminesulphonate corresponds with mono-nitric peroxide, and its crystalline form with di-nitric peroxide. Since then, Piloty and Schwerin (*loc. cit.*) have expressed the belief that *porphyrexide*, which has the colour of mono-nitric peroxide, may also be a derivative of this peroxide, because it contains the group :NO singly, as shown by the formula  $(\text{C}_5\text{H}_9\text{N}_3):\text{NO}$ . Its molecular weight, however, has been only indirectly ascertained, that is, by cryoscopic determinations of those of its nitrate and its chloro-derivatives. That its molecular weight is not double as great is a remarkable fact, for, in its chemical behaviour, and especially in its reversible relation with *porphyrexine*,  $(\text{C}_5\text{H}_9\text{N}_3):\text{NOH}$ , porphyrexide seems to belong to the class of oxime-peroxides. Piloty and Schwerin do not indeed recognise this, and have instead come to the conclusion that the nitrogen of the group :NO in porphyrexide and in mono-nitric peroxide must be quadrivalent. In the light of Haga's experimental results, this view of the matter has become untenable, since porphyrexide and the peroxyaminesulphonates appear to belong to the same class of nitroxy-compounds, as Piloty and Schwerin themselves have pointed out.

In the few cases in which it has been possible to determine

cryoscopically the molecular weight of a glyoxime-peroxide, this has been found to include :NO twice. This result may be owing to the glyoxime constitution of these peroxides, but, even so, there is still no peroxide, except mono-nitric peroxide, and possibly porphyrexide, the molecular weight of which is such that it contains the group :NO only once. The occurrence of many nitroso-compounds in a colourless, solid form, and in a bluish-violet liquid form, does not lend much assistance in deciding the molecular weights of the two forms of a peroxyaminesulphonate, since they contain not :NO but ·NO. But it must not be left out of sight that Piloty (who thinks otherwise, and has been followed by Schmidt, Bamberger, and others) has succeeded in showing that the white form of these compounds contains the group ·NO twice, and that the deeply-coloured modification contains it only once. But here the latter is the form which must be treated as the chemically active one, whilst the double weight found for the white form has to be left uninterpreted chemically, as, for example, in the case of the formula  $(C_8H_{17}NO)_2$  for nitroso-octane.

In the paper by Hantzsch and Semple (*loc. cit.*), there occurs, but in a foot-note only and without comment or explanation, the punctuated formula  $O:N:(SO_3K)_2$ ; whether this is to be regarded as a printer's error for  $O:N:(SO_3K)_2$  is uncertain, but if it is not, it indicates some recognition by these chemists of the presence of univalent oxygen. However this may be, the possibility of the nitrogen being quadri-valent being inadmissible, the only solution of the matter seems to be to consider that both mono-nitric peroxide and porphyrexide are compounds of univalent oxygen, although still peroxides. The fact that a molecular quantity, such as that formulated by  $HO, NO_2, (SO_3K)_2NO$ , or  $(C_5H_9N_2)NO$ , is never met with singly in chemical interactions militates against the acceptance of this explanation. Piloty and Schwerin, in discussing the quadrivalency of nitrogen, conceal this fact by stating that porphyrexide is produced from porphyrexine by the action of *half an atom* of oxygen. It is much more correct to hold with Haga that the molecule of peroxyaminesulphonate, and therefore also of mono-nitric peroxide and of porphyrexide, is not less than that represented by  $[NO(SO_3K)_2]_2, (NO_2)_2$ , or  $(C_5H_9ON_4)_2$ , as the case may be, if by molecule is meant the smallest chemically active weight of a substance. But still the fact remains that, when measured by comparison of their physical properties, the molecular weights of porphyrexide and red nitric peroxide are expressed by half the above formulæ, and that probably the bluish-violet form of a peroxyaminesulphonate has also a molecular weight, which, when physically considered, should be expressed by the formula  $NO(SO_3K)_2$ . These weights, only physically determined, have no chemical significance, and should be distinguished from their doubles, the truly chemical molecular weights. But, as

pseudo-chemical molecules, they must be represented as containing a univalent atom of oxygen.

It is, after all, not so difficult to admit that oxygen may be univalent in a peroxide. In fact, a true peroxide may be defined and differentiated from other oxides, as being a compound in which some or all of the oxygen is exerting on the rest of the compound only half its usual valency. Or, conversely, a peroxide may be defined as a compound containing oxygen which is either actually univalent or exterior and quasi-univalent. Apart from the unfamiliar nature of the conception of actually univalent oxygen, it seems natural enough to find a normal molecule of nitric peroxide dissociate at a gentle heat into two identical but simpler ones, in consequence of the linked oxygen atoms becoming parted and losing valency. On the other hand, the assumption that nitrogen is quadrivalent does not accord with the result actually obtained, when by cooling nitric peroxide it is found that the valency of the nitrogen decreases instead of increasing,  $2\text{O}:\text{N}:\text{O}$  becoming  $\text{O}:\text{N}\cdot\text{O}\cdot\text{O}:\text{N}:\text{O}$ .

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### XIII.—*The Solubility Curves of the Hydrates of Nickel Sulphate.*

By BERTRAM DILLON STEELE, D.Sc., and F. M. G. JOHNSON.

THE experiments recorded in this paper were undertaken with the object of determining the conditions of equilibrium and the composition of the phases in the two component system, nickel sulphate—water.

Hydrates of nickel sulphate have been described containing 1, 2, 6, and 7 molecules of water. The heptahydrate, which is found in nature as the mineral moresonite, may be obtained by crystallisation at the ordinary temperature from neutral solutions of the salt. It occurs in the form of pale green, rhombic crystals isomorphous with heptahydrated magnesium sulphate, and on prolonged exposure to the atmosphere becomes changed into aggregates of blue crystals having the composition  $\text{NiSO}_4\cdot 6\text{H}_2\text{O}$ . This change has, for a long time, been regarded as being brought about by the action of sunlight (Phillips and Cooper, *Poggendorff's Annalen*, 1879, 6, 194), but Dobrosserdoff (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 300) has recently shown that this is not the case, since sunlight has no effect on the heptahydrate, provided that the crystals are contained in a space saturated with water vapour and maintained at a low temperature; accordingly the

reaction in question is a simple case of efflorescence. The same hexahydrate was obtained by Brooke and Phillips (*loc. cit.*) and by Pierre (*Ann. Chim. Phys.*, 1846, [iii], 16, 252) in the form of blue, tetragonal crystals by crystallisation at the ordinary temperature from a solution containing sulphuric acid, and by Marignac and Mitscherlich from neutral solutions at about 40°.

Isothermal crystallisation of neutral solutions at temperatures between 60° and 70° yields a bright green, monoclinic salt which also contains 6 molecules of water.

The dihydrate is described by Étard (*Compt. rend.*, 1878, 87, 602) as being formed by the action of strong sulphuric acid on the hexa- or hepta-hydrates, and Lescœur (*Chem. Centr.*, 1895, i, 525) states that by adding concentrated sulphuric acid to a solution of nickel sulphate, a precipitate of the monohydrate is obtained.

The study of the solubility curves of nickel sulphate between -5° and 100° has not indicated the existence of any hydrate containing less than 6 molecules of water of crystallisation. Solubility determinations have not been made at temperatures above 100°, but from the curves of Étard and Engel (*Compt. rend.*, 1888, 106, 206) there appears to be a transition point at about 118°, and on analysing the solid phase separating at 131°, we found it to be the dihydrate,  $\text{NiSO}_4 \cdot 2\text{H}_2\text{O}$ .

The solubility of nickel sulphate has been determined at various temperatures by Tübler (*Annalen*, 1855, 95, 193). His results, however, differ considerably from ours, and are not sufficiently numerous to indicate the position of the various transition points.

#### *Preparation of the Hydrates.*

The heptahydrate was prepared by twice recrystallising the ordinary salt and shown to be pure by analysis. The salt used in estimating the solubilities at a few temperatures was prepared by precipitating a saturated aqueous solution with alcohol, and was thus obtained in the form of very small, green, granular crystals containing 21.12 per cent. of nickel, the calculated value being 20.91.

The foregoing salt, when left in contact with its saturated solution for some hours at any temperature between 32° and 53°, is converted into the blue hexahydrate, which was analysed with the following result: Found Ni = (1) 22.54; (2) 22.41.

$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  requires Ni = 22.23 per cent.

The blue hexahydrate, employed in the experiments made between 32° and 53°, was prepared by the slow evaporation at the ordinary temperature of solutions containing 30 per cent. of sulphuric acid.

The large crystals thus obtained were powdered and thoroughly washed with a saturated solution of nickel sulphate in order to remove sulphuric acid.

If the heptahydrate or the blue hexahydrate is left in contact with the saturated solution at temperature above  $54^{\circ}$ , it very rapidly becomes converted into the bright green, monoclinic salt which, on analysis, was found to have the same composition as the blue tetragonal hydrate.

Found, Ni = (1) 22.55 ; (2) 22.50.

$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  requires Ni = 22.23 per cent.

In order to determine the composition of the solid phase, which is present at temperatures above  $118^{\circ}$ , a quantity of the dry hexahydrate was sealed up in a thick walled glass tube and heated for some hours at  $131^{\circ}$ . A little below this temperature, the substance partially melted with the formation of a clear green solution and a dull yellowish-green, amorphous solid, for the separation of which the following method was adopted. The tube containing the mixture was carefully inverted, so that the greater part of the liquid drained away from the powder. After cooling in this position, it was cut into two parts, and the solid, placed on pieces of porous tile, was sealed up in another tube and again heated at  $131^{\circ}$ . The adherent liquid portion, which had solidified on cooling, again liquefied and was absorbed by the porous tile, leaving the new salt practically dry and pure, as indicated by the following analysis :

Found, Ni = (1) 30.8 ; (2) 30.87.

$\text{NiSO}_4 \cdot 2\text{H}_2\text{O}$  requires Ni = 30.87 per cent.

#### *Solubility Determinations.*

The solubilities were determined by enclosing the salt, with the requisite amount of distilled water, in tubes provided with well-fitting india-rubber stoppers. The tubes were attached to a shaking apparatus driven by a Henrici hot-air motor, and immersed in a thermostat provided with a toluene gas regulator, by means of which the temperature could be kept constant to a tenth of a degree. Preliminary experiments having shown that equilibrium was reached in about 12 hours, the tubes were shaken for twice that time to ensure saturation.

The solutions were filtered within the thermostat in the following manner. The india-rubber stopper in the solubility tube contained a hole, which was closed with a glass rod during the shaking. When it was desired to filter the solution, the rod was withdrawn, and in its place was inserted a piece of glass tubing with a small bulb blown in

the centre, this bulb being packed with asbestos to serve as a filter. The other end of the tube passed through an india-rubber stopper, which fitted into a weighing bottle, and through which passed a glass tube long enough to reach out of the thermostat. The solubility tube was thus attached to a weighing bottle by a filtering tube, and by inverting the two and applying suction to the projecting tube, the solution was filtered without having been for an instant removed from the bath. The filtrate in the weighing bottle was weighed and diluted to 500 c.c., a convenient portion of this solution being taken for analysis.

The nickel was estimated electrolytically, using a current density of 0.5 ampere, 8 to 10 hours being required for the electrolysis, which was carried out in a solution containing ammonium sulphate and excess of ammonia.

All the solubility results (with the exception of those at  $0^{\circ}$  and  $-5^{\circ}$ ) are the mean values of at least two closely concordant determinations carried out in different vessels.

Of the experiments recorded in Table I, the first was carried out in

TABLE I.\*

(1) The solubility curve of  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ .

Salt used.	Temperature.	Concentration.	Salt remaining.
1. $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	$-5^{\circ}$	25.74	$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$
2. —	0	27.22	—
3. —	9	31.55	—
4. —	15	34.19	—
5. —	22.6	37.90	—
6. —	22.8	38.88	—
7. —	30.0	42.46	—
8. $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	30.0	42.47	—
9. $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	32.3	44.02	$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$
10. $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	32.3	43.57	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$
11. $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	33.0	45.74	$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$
12. $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	33.0	43.35	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$
13. $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	34.0	45.5	$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$
14. „	34.0	43.84	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$
15. $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	34.0	43.82	—

\* In this and the other tables in the paper, concentrations are expressed as parts by weight dissolved in 100 grams of water.

a bath of brine surrounded by a mixture of powdered ice and salt, and maintained at a constant temperature by allowing a very slow current of warm brine to circulate through the bath. The second experiment was carried out in a bath of melting ice. For temperatures

below  $30^{\circ}$ , the heptahydrate only was used in determining the solubilities. For temperatures between  $30^{\circ}$  and  $34^{\circ}$ , a number of experiments were made, using both the heptahydrate and the blue hexahydrate in the hope that a portion of each curve extending beyond the transition point might be realised. This has been done for the heptahydrate, the metastable portion of the curve being represented by experiments 9, 11, and 14, in Table I, which give solubilities of the heptahydrate at temperatures close to the point of transition of this hydrate into the hexahydrate.

In experiment 8, in which the solid phase was originally the blue hexahydrate, transformation rapidly took place into the green heptahydrate, and although many attempts were made, it was not found possible to obtain the metastable portion of the curve for the hexahydrate.

In the accompanying diagram (p. 118), the experiments from this table are represented by the curve ABC.

TABLE II.

Solubility curve of  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  (blue tetragonal).

Salt used.	Temperature.	Concentration.	Salt remaining.
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (blue)	$32.3^{\circ}$	43.57	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (blue)
"	$33.0$	43.35	—
$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	$34.0$	43.84	—
"	$35.6$	43.79	—
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	$44.7$	48.05	—
$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	$44.7$	47.97	—
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (blue)	$50.0$	50.15	—
—	$51.0$	50.66	—
—	$52.0$	52.34	—
—	$53.0$	52.34	—
—	$54.5$	52.5	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (green)

On plotting the results collected in Tables I and II, the two curves are found to intersect between  $31^{\circ}$  and  $32^{\circ}$ . The transition point corresponding with the change  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O} \rightleftharpoons \text{NiSO}_4 \cdot 6\text{H}_2\text{O} + \text{saturated solution}$  therefore lies very near to  $31.5^{\circ}$ . In order to confirm this point and in the hope of determining it with greater accuracy, experiments were carried out with a dilatometer, which assumed the usual form of a large thermometer with a graduated stem partially filled with a mixture of the heptahydrate, the blue tetragonal hexahydrate, and a certain amount of *m*-xylene. The vessel, being exhausted to remove air bubbles from the salt, was then filled to the

required position with more of the hydrocarbon and placed in a bath at  $30^{\circ}$ . The temperature was now allowed to rise very slowly; a steady increase of volume occurred up to  $31.4^{\circ}$ , when there was a sudden break followed by a much smaller increase as the temperature was raised still further. The transition point may therefore be taken as lying between  $31.4^{\circ}$  and  $31.6^{\circ}$ .

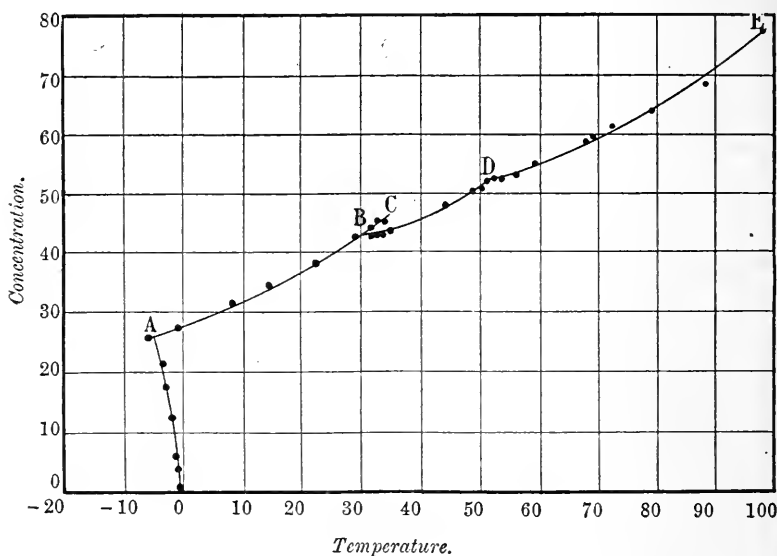


TABLE III.

Solubility curve of  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  (green monoclinic).

Salt used.	Temperature.	Concentration.	Salt used.	Temperature.	Concentration.
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (blue)	$54.5^{\circ}$	52.50	$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	$70.0^{\circ}$	59.44
$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ }	$57.0$	53.40	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (blue)	$73.0$	60.72
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (blue)	$60.0$	54.84	$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ }	$80.0$	63.17
$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	$69.0$	58.38	"	$89.0$	67.90
"			"	$99.0$	76.71

Throughout the series of determinations indicated in Table III, the remaining salt is the green, monoclinic hexahydrate.

The solubility data obtained in the neighbourhood of  $52^{\circ}$  indicate a

break in the curve, due to a second transition point. This inflexion, which is very slight and might be easily overlooked, is confirmed by the appearance of the residual solid phase after equilibrium is established. If we start with the blue, tetragonal hexahydrate, at temperatures above  $53^{\circ}$  a very rapid change takes place, the blue substance giving place to a bright green solid having the same composition. On the other hand, this green salt is rapidly converted at temperatures slightly below  $53^{\circ}$  into the blue modification, and on plotting, on a large scale, the results given in Tables II and III, the two curves are found to cut each other very close to  $53^{\circ}$ . In order to confirm this conclusion, experiments were made with a dilatometer containing initially the blue hexahydrate mixed with a small quantity of the green salt. No indication of a break could be detected until the mixture was heated for some time at  $70^{\circ}$ , when the salt was seen to have changed into the green modification. The dilatometer was then placed in a bath at  $56^{\circ}$  and allowed to cool slowly, when there was a steady contraction down to  $54.0^{\circ}$ , then little or no contraction until  $53.3^{\circ}$ , and then a steady contraction, but less than the original diminution. A duplicate experiment confirmed this result and also failed to detect any break on slowly raising the temperature from a point below  $53^{\circ}$ . According to this result, the temperature corresponding with the change  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  (blue tetragonal)  $\rightleftharpoons$   $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  (green monoclinic) lies between  $53.3^{\circ}$  and  $54^{\circ}$ . The solubilities give this temperature as lying near  $53^{\circ}$ , and  $53.3^{\circ}$  is probably not far from the true transition point.

Since the solubility curves of the three salts,  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  (blue), and  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  (green), lie so nearly in a straight line, it was thought that possibly a break in the curve between  $55^{\circ}$  and  $100^{\circ}$  might have been overlooked.

In order to test this, analyses of the undissolved salt were made at  $60^{\circ}$ ,  $70^{\circ}$ , and  $89^{\circ}$ , and in all cases the salt was found to be the hexahydrate. Moreover, the solid phase at all temperatures between the above limits has the bright green colour characteristic of the monoclinic hexahydrate. In the analysis of the solutions at  $89^{\circ}$  and  $99^{\circ}$ , the saturated solution was separated from the undissolved salt by the method of decantation in a bent tube employed by Étard and Engel (*loc. cit.*).

#### *Ice Curve and Cryohydrate Point.*

The ice curve was determined by measuring the temperature at which ice began to separate from solutions of nickel sulphate of known concentration, the measurements being carried out in a Beckmann freezing point apparatus.

The temperatures and concentrations from which the curve has been plotted are as follows:

Temperature.....	-0.47°	-0.72°	-1.46°	-2.15°	-2.85°
Concentration .....	3.35	5.53	11.97	17.23	21.18

The cryohydrate point was fixed in the following manner. A solution containing about 30 parts of the anhydrous sulphate,  $\text{NiSO}_4$ , to 100 parts of water was placed in the inner tube of the Beckmann apparatus, which was surrounded with a freezing mixture maintained at about  $-5^\circ$ , and the steady temperature at which ice and nickel sulphate separated was found to be  $-4.15^\circ$ .

### *Summary.*

The following is a summary of the results obtained with the system, nickel sulphate—water.

#### *(1) Quadruple Points.*

A. Cryohydrate point of the heptahydrate [ $-4.15^\circ$ ].

B. Transition point: heptahydrate  $\rightleftharpoons$  hexahydrate (blue) + saturated solution [ $31.5^\circ$ ].

D. Transition point: hexahydrate (blue)  $\rightleftharpoons$  hexahydrate (green) [ $53.3^\circ$ ].

Transition point: hexahydrate (green)  $\rightleftharpoons$  dihydrate + saturated solution (not accurately determined).

#### *(2) The Equilibrium Curves.*

The curves OA, ABC, BD, and DE in the diagram correspond with the solid phases: ice; the heptahydrate,  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ ; the blue hexahydrate,  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ ; and the green monoclinic hexahydrate,  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ , respectively.

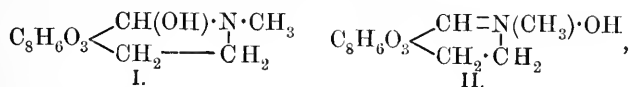
MACDONALD CHEMISTRY BUILDING,  
MCGILL UNIVERSITY,  
MONTREAL.

#### XIV.—*The Relative Strengths of the Alkaline Hydroxides and of Ammonia as Measured by their Action on Cotarnine.*

By JAMES JOHNSTON DOEBBIE, M.A., D.Sc., ALEXANDER LAUDER, B.Sc., and CHARLES KENNETH TINKLER, Research Student of the University of Edinburgh.

IN a paper recently communicated to the Society (Trans., 1903, 83, 598), it was shown that the spectra of cotarnine in ethereal or chloroform solution, of cyanohydrocotarnine and of ethoxyhydrocotarnine are identical or nearly so with those of hydrocotarnine and its salts, whilst the spectra of dilute aqueous or alcoholic solutions are identical with those of the cotarnine salts. From this, it was argued that the substances in the first group are all constituted like hydrocotarnine, those in the second being like the cotarnine salts. This conclusion is supported by the fact that, whilst the substances in the first group are colourless, those in the second are yellow. It was further shown that an ethereal or chloroform solution of cotarnine becomes yellow when treated with alcohol and gives absorption spectra which approach more and more nearly to those of the cotarnine salts as the quantity of alcohol is increased. On the other hand, when an aqueous solution is treated with sodium hydroxide or other soluble base, the reverse change takes place and the yellow colour gradually disappears; the proportion of cotarnine which undergoes this change depending on the amount of basic hydroxide present. It was suggested that a fuller study of these reactions might throw light on the conditions of isomeric and tautomeric changes generally, and that it might be possible to use the action of the bases on cotarnine as a means of comparing their strengths. In the present paper, we propose to give the results of some preliminary experiments on the latter subject.

In our former paper, an account was given of the absorption curves of the two forms of cotarnine (Figs. I and II):



and photographs of the spectra were reproduced in Plates I and II (carbinol and ammonium forms respectively), which accompany the paper. Reference to these photographs will show that the spectra of the two forms are highly characteristic.

The change which cotarnine in aqueous solution undergoes when

acted on by sodium hydroxide depends, as already stated, on the quantity of this reagent present. After the addition of any given quantity of the hydroxide, a state of equilibrium between the two forms of cotarnine is established almost instantaneously and, provided that the temperature is kept constant, no further change takes place, at any rate in moderately dilute solutions, even after a lapse of several hours. Each additional quantity of sodium hydroxide causes a further change until the ammonium form is all converted into the carbinol form. This is practically the case when a milligram-molecule of cotarnine is dissolved in one litre of a normal solution of sodium hydroxide. By photographing the spectra of the solution after each addition of the alkali hydroxide, the change from the one form to the other can be followed through all its phases. Figs. 17—24 of Plate III, accompanying the paper already quoted, show generally how the spectra of the ammonium form change into those of the carbinol form as the quantity of sodium hydroxide is increased. The spectra thus obtained are in fact the spectra of mixtures of the two forms and can all be reproduced exactly by mixing together hydrocotarnine hydrochloride and cotarnine hydrochloride in the proper proportions. By preparing a series of such mixtures containing the two substances in known proportions, it is possible, from a comparison of their spectra with the spectra of an aqueous solution of cotarnine, which has been acted on by sodium hydroxide, to determine the amount of the ammonium form which has been changed into the carbinol form. By using other soluble bases in place of sodium hydroxide, the data are obtained which are required for a comparison of their strengths. As already stated, the action of bases on cotarnine is so rapid that no comparison of their strengths, founded on the amount of change produced by equimolecular quantities in a given time, is possible. Temperature has a considerable influence on the action, and consistent results can only be obtained when the experiments are carried out at the same temperature.\*

It will be seen from the tabulated comparison of the results obtained at 12° and 18° respectively (Table I) that the effect of heating is to diminish the action of the alkalis, a given quantity at the higher temperature producing a smaller effect than the same quantity at the lower temperature. The results are represented graphically in the accompanying curve (p. 123).

\* The results given in our previous paper were obtained at the ordinary temperature, without precautions being taken to ensure that the temperature was always the same. They therefore differ somewhat from those given in the present paper.

CURVE I.

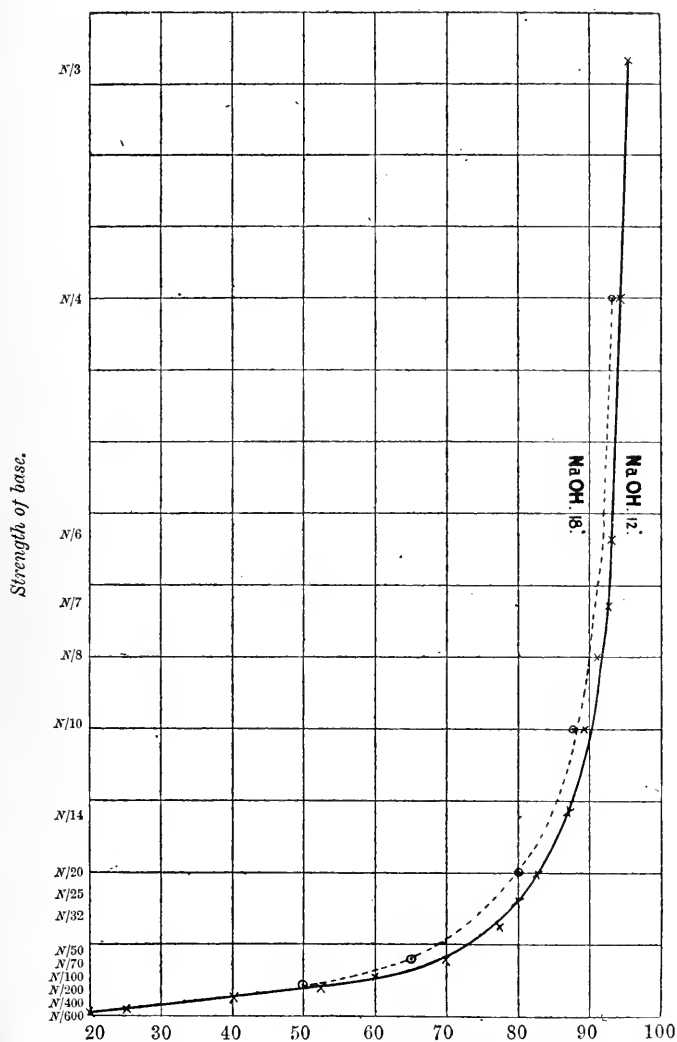
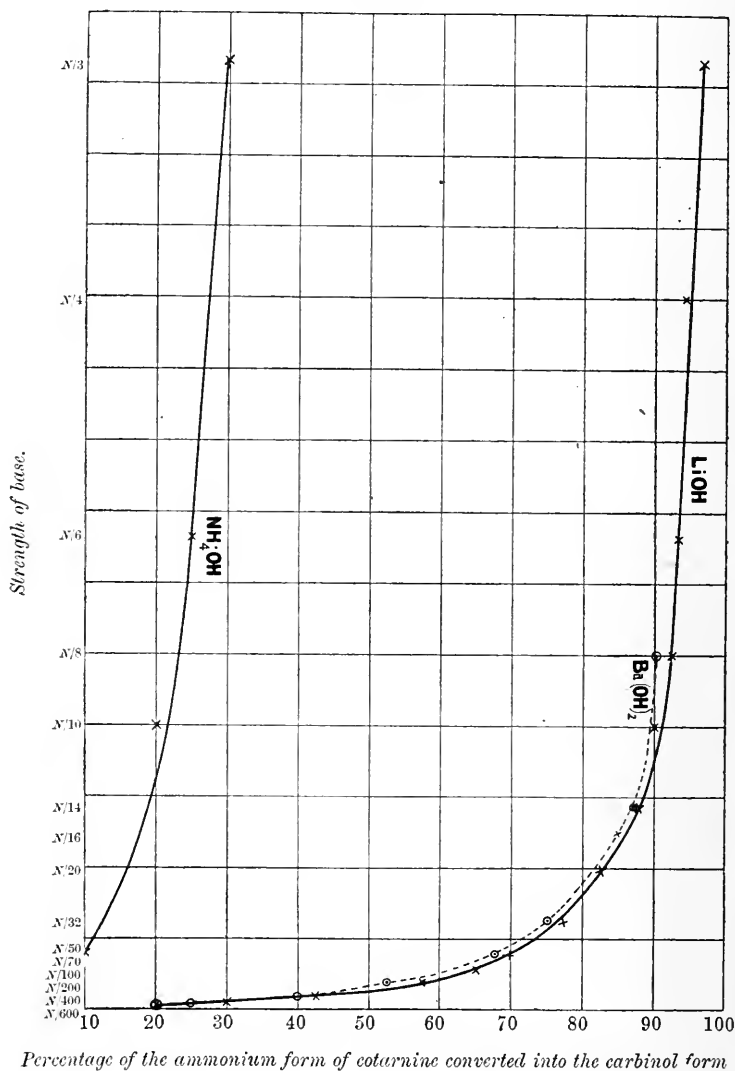


TABLE I.

Strength of sodium hydroxide.	Percentage of carbinol form produced.	
	At 12°.	At 18°.
N/4	94	93
N/10	89	87.5
N/20	82.5	80
N/50	70	65
N/100	52.5	50

In Table II, the results obtained at  $12^\circ$  by the action of equimolecular solutions of the hydroxides of the alkali and alkaline earth metals and ammonia are given, and the results are represented graphically in the accompanying curve. The percentages give the amount of ammonium form which is converted into the carbinol form.

CURVE II.



Percentage of the ammonium form of cotarnine converted into the carbinol form

TABLE II.

Strength of base.	KOH.	LiOH.	NaOH.	Ba(OH) <sub>2</sub> .	Ca(OH) <sub>2</sub> .	NH <sub>4</sub> ·OH.
<i>N</i>	98·5	98·5	98·5	—	—	45
<i>N/2</i>	97·5	97·5	97	—	—	40
<i>N/3</i>	96·5	96·5	95·5	—	—	30
<i>N/4</i>	95	94	94	—	—	—
<i>N/6</i>	93	93	93	—	—	25
<i>N/7</i>	92·5	—	92·5	—	—	—
<i>N/8</i>	91	92·5	91	90	—	—
<i>N/10</i>	89	90	89	—	—	20
<i>N/14</i>	88	88	87·5	87·5	—	—
<i>N/16</i>	—	85	—	—	—	—
<i>N/20</i>	83	82·5	82·5	—	—	—
<i>N/25</i>	—	—	80	—	—	—
<i>N/32</i>	77·5	77·5	77·5	75	72·5	—
<i>N/50</i>	67·5	70	70	67·5	67·5	10
<i>N/70</i>	62·5	65	60	—	—	—
<i>N/100</i>	52·5	57·5	52·5	52·5	50	—
<i>N/200</i>	42·5	42·5	40	40	40	—
<i>N/400</i>	25	30	25	25	25	—
<i>N/600</i>	20	20	20	20	20	—

The hydroxides of lithium, sodium, and potassium give nearly identical curves, showing that, so far as this reaction is concerned, they all have nearly the same strength. It is not possible to get a sufficient quantity of calcium or barium hydroxide into solution in one litre of water to convert a milligram-molecule of cotarnine entirely into the carbinol form, but that portion of the curve which can be drawn for these bases approximates closely to the corresponding portion of the curve for the hydroxides of the alkali metals, the slight difference between the curves indicating that the hydroxides of the alkali metals are the stronger. Some experiments were made with thallium hydroxide, but, as solutions of this substance themselves possess considerable absorptive power, trustworthy results could only be obtained with dilute solutions. These data indicate that thallium hydroxide is a weaker base than the alkali hydroxides, but very much stronger than ammonia. A very concentrated solution of ammonia (more than nine times the strength of a normal solution) is required to convert the ammonium form of cotarnine entirely into the carbinol form. We propose to discuss the case of ammonia more fully in connection with investigations on the alkylated ammonias.

The general result of our experiments is to show that in their action on cotarnine, the bases have the same relative strengths as in other reactions. The curves representing the relation between the amount

of change and the quantity of base producing it are apparently hyperbolic, but we have so far been unable to find an equation for them.

The action of sodium hydroxide on an aqueous solution of cotarnine is capable of explanation in terms of the dissociation theory of electrolytes. Cotarnine in dilute aqueous solution is a strong electrolyte (Hantzsch and Kalb, *Ber.*, 1899, 23, 3109). It may, therefore, be assumed that the solution contains a mixture in equilibrium of the undissociated ammonium form together with the hydroxyl and other ion resulting from its dissociation, with practically none of the carbinol form. By the addition of sodium hydroxide the active mass of the hydroxyl ions is increased and the dissociation of the ammonium form is diminished. The ammonium form then passes into the carbinol form, in which dissociation is at a minimum, until the equilibrium is restored. The further addition of sodium hydroxide leads to a repetition of these changes until, when the solution is normal, the ammonium form is practically all converted into the carbinol form. A very small quantity of sodium hydroxide produces no appreciable effect on an aqueous solution of cotarnine, but we have not found it possible to determine with accuracy the exact point at which the solutions are isohydric.

#### *Experimental Details.*

The determinations of the percentages of the ammonium form of cotarnine converted into the carbinol form, which are given in this paper, were made by comparing photographs of the absorption spectra\* of cotarnine in solution in sodium hydroxide, or other soluble base, with standard photographs of mixtures containing hydrocotarnine hydrochloride and cotarnine hydrochloride in known proportions. In the preparation of the standard series of mixtures used for this purpose, a solution containing 1 milligram-molecule of hydrocotarnine hydrochloride dissolved in one litre of water was taken as the starting point. This was mixed with a solution of cotarnine hydrochloride of the same equivalent strength in the proportions required to give a solution containing 97.5 per cent. of hydrocotarnine hydrochloride and

\* The method of photographing absorption spectra which we employ has already been sufficiently explained in former papers, see especially *Trans.*, 1889, 55, 649, and the papers by Hartley therein cited. The reference lines employed were those given by an alloy of cadmium, tin, and lead. The photographs of the spectra, from which the data discussed in this paper have been derived, have not been reproduced as illustrations on account of the difficulty of obtaining reproductions sufficiently delicate to show the details of the spectra on which their accurate comparison is based. So far as photographs are necessary for the elucidation of the paper, this purpose is served by those already published (Dobbie, Lauder, and Tinkler, *loc. cit.*).

2.5 per cent. of cotarnine hydrochloride. The proportion of cotarnine hydrochloride to hydrocotarnine hydrochloride was increased by 2.5 per cent. at a time until a solution containing 97.5 per cent. of the former and 2.5 per cent. of the latter was reached. The absorption spectra of these mixtures form a graduated series between the spectra characteristic of the two forms of cotarnine. The series of standard photographs having been prepared, it is easy to estimate the amount of change produced in an aqueous solution of cotarnine by any given quantity of a soluble base, by photographing the spectra of the solution and comparing the photographs with those of the reference series. If the photograph to be determined does not coincide exactly with any in the reference series, its position between two successive mixtures can always be found. A number of intermediate mixtures are then photographed until a photograph is obtained which exactly corresponds with the one under examination, the exact composition of the mixture in question being thus determined. In preparing the series of reference photographs, hydrocotarnine hydrochloride was preferred to the cyanohydrocotarnine formerly employed, on account of its greater stability and because of its solubility in water. These two substances have the same spectra.

The spectra of mixtures of hydrocotarnine hydrochloride with cotarnine hydrochloride are identical with those obtained by passing the light through an equal thickness of the two solutions contained in separate cells. Thus the spectrum obtained by passing the light through a 20 mm. layer of a mixture of hydrocotarnine hydrochloride and cotarnine hydrochloride solutions, in equal proportions, is identical with that obtained by passing it in succession through two cells each containing a layer 10 mm. thick of one of the solutions. The same result is obtained by using a 10 mm. cell filled with an aqueous solution of cotarnine and another cell of equal thickness containing a concentrated sodium hydroxide solution of cotarnine. These results were confirmed by numerous experiments, in which layers of various thicknesses were employed. In these experiments, the thickness of quartz employed was the same; when this precaution was not observed, the accuracy of the comparison was interfered with by the slight absorption due to the quartz plates.

We hope to render the foregoing method more accurate by a modification of our apparatus, and by using hydrastinine in place of cotarnine. With cotarnine, it is quite easy, in some parts of the series of mixtures of the two forms, to detect differences of 0.5 per cent. with certainty, but in mixtures containing a large proportion of the ammonium form it is not possible to detect with accuracy, differences of less than 2.5—5.0 per cent. The spectra of the ammonium form hydrastinine are more complicated than those of the corresponding

form of cotarnine, and admit of much smaller differences being readily distinguished.

We have to express our thanks to Professor Crum Brown and to the authorities of the University of Edinburgh for kindly affording us facilities for conducting part of this work in the University laboratory; and to Professor W. N. Hartley for the use of the apparatus with which the experiments were carried out.

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XV.—*aa-Dimethylbutane- $\alpha\beta\delta$ -tricarboxylic Acid,  $\gamma$ -Keto- $\beta\beta$ -dimethylpentamethylene- $\alpha$ -carboxylic Acid, and the Synthesis of Inactive  $\alpha$ -Campholactone of Inactive  $\alpha$ -Campholytic Acid and of  $\beta$ -Campholytic Acid (isoLauronic Acid).*

By WILLIAM HENRY PERKIN, jun., and JOCELYN FIELD THORPE.

DURING the course of a long series of researches on the constitution of camphor and its derivatives, attention has been repeatedly directed to the advisability of synthesising the more important substances obtained by the degradation of camphor, in order, thus, to definitely establish their constitution. It has frequently been found that analytical methods have, alone, not been sufficient to prove the constitutions of such degradation products, and in the more difficult cases, as, for example, in the determination of the constitutions of camphoronic and isocamphoronic acids, a definite proof was first obtained by synthetical means (Perkin and Thorpe, *Trans.*, 1897, 71, 1169; 1899, 75, 897; Perkin, *Trans.*, 1902, 81, 246).

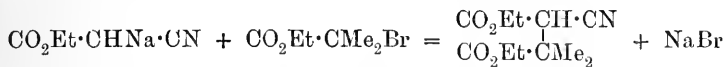
In continuing our experiments in this direction, we have endeavoured to find some means of synthesising, not only open chain acids, such as those mentioned above, but also closed chain compounds more closely allied to camphor and camphoric acid. We hope that it may eventually be found possible to prepare these substances themselves, in quantities sufficient for definite identification, by synthetical means, but the problem is an exceedingly difficult one.\*

In the present paper, we describe a series of reactions which has led

\* This investigation, an abstract of which appeared in the *Proceedings*, 1903, 19, 61, was completed and this paper written before the publication of G. Komppa's complete synthesis of camphoric and dehydrocamphoric acids (*Ber.*, 1903, 36, 4332).

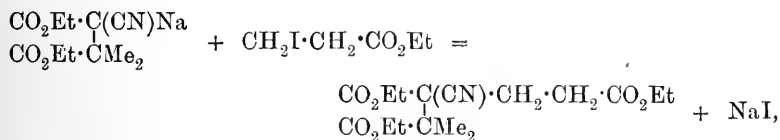
to the synthesis of inactive  $\alpha$ -campholytic acid, and indirectly to that of  $\beta$ -campholytic acid (*isolaunolic acid*).

When ethyl cyanoacetate is digested in alcoholic solution with sodium ethoxide and ethyl bromoisobutyrate, sodium bromide separates and ethyl cyanodimethylsuccinate is formed, thus :



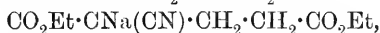
(compare Bone and Sprankling, *Trans.*, 1899, **75**, 854).

The sodium compound of this cyano-ester interacts readily with ethyl  $\beta$ -iodopropionate, forming *ethyl  $\beta$ -cyano- $\alpha\alpha$ -dimethylbutane- $\alpha\beta\delta$ -tricarboxylate*,

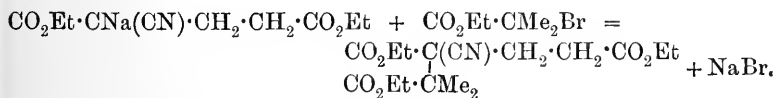


but, unfortunately, during this reaction, a large amount of the  $\beta$ -iodopropionic ester is decomposed with the elimination of hydrogen iodide and formation of ethyl acrylate,  $\text{CH}_2\text{:CH}\cdot\text{CO}_2\text{Et}$ , and by no variation in conditions could this be avoided. This loss of valuable material would have made further progress impossible had it not been discovered that the acrylate thus produced may be converted into ethyl cyanodimethylbutanetricarboxylate by the following series of reactions.

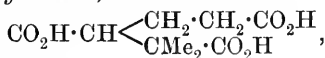
Ethyl acrylate condenses with the sodium compound of ethyl cyanoacetate, yielding the sodium compound of ethyl  $\alpha$ -cyanoglutarate, thus:  $\text{CO}_2\text{Et}\cdot\text{CHNa}\cdot\text{CN} + \text{CH}_2\text{:CH}\cdot\text{CO}_2\text{Et} =$



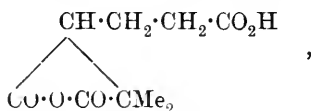
an ester which had already been prepared by L. Barthe (*Compt. rend.*, 1894, **118**, 1268) from the sodium compound of ethyl cyanoacetate and ethyl  $\beta$ -bromopropionate. The sodium compound of ethyl  $\alpha$ -cyanoglutarate, when digested in alcoholic solution with ethyl  $\alpha$ -bromoisobutyrate, gives a good yield of ethyl cyanodimethylbutanetricarboxylate,



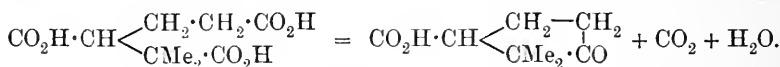
When boiled with hydrochloric acid, this cyano-ester is hydrolysed with the elimination of carbon dioxide and formation of  *$\alpha\alpha$ -dimethylbutane- $\alpha\beta\delta$ -tricarboxylic acid*,



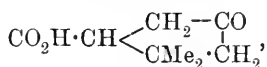
a crystalline, readily soluble acid which melts at 155—157°. When this acid is distilled under reduced pressure, it loses water and is converted into the *internal*  $\alpha\beta$ -anhydride of dimethylbutanetricarboxylic acid,



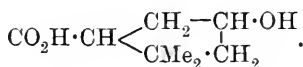
which melts at 98° and dissolves in water, regenerating the tribasic acid. If the dry sodium salt of the acid is heated with acetic anhydride at 140°, carbon dioxide is evolved and a new acid is produced,\* decomposition taking place according to the equation:



The  $\gamma$ -keto- $\beta\beta$ -dimethylpentamethylene- $\alpha$ -carboxylic acid thus obtained melts at 109—110° and yields an oxime and a sparingly soluble semicarbazone; it is isomeric with, and very closely allied to, the  $\delta$ -keto- $\beta\beta$ -dimethylpentamethylene- $\alpha$ -carboxylic acid,



which Perkin and Thorpe (Trans., 1901, 79, 782) obtained by the reduction of dimethylketodicyclopentanedicarboxylic acid, and which melts at 103°. The latter acid is not easily acted on by sodium amalgam, but if a large excess is employed, it is ultimately reduced to the corresponding hydroxydimethylpentamethylenecarboxylic acid (m. p. 115°):

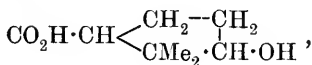


This acid must exist in *trans*- and *cis*-modifications, the latter of which should, like all *cis*- $\gamma$ -hydroxy-acids, readily yield a lactone, and since the acid (m. p. 115°) which was actually obtained showed no tendency to lose water with formation of a lactone, it is evidently the *trans*-modification.

On the other hand, it is interesting to note that the  $\gamma$ -keto-acid (m. p. 110°), unlike the  $\delta$ -keto-acid (m. p. 103°), is not reduced at all even when the aqueous solution of its sodium salt is boiled with a large excess of sodium amalgam, and this difference in behaviour is doubtless due to the proximity of the  $>\text{CMe}_2$  complex to the keto-

\* If this curious reaction should prove to be a general one, it will afford a convenient means of synthesising many important closed chain keto-acids and, for this reason, experiments are being carried out by one of us with the object of ascertaining the exact conditions under which the change takes place.

group in the latter case. Reduction of the  $\gamma$ -keto-acid may, however, be effected by adding sodium to the boiling alcoholic solution of the acid, when an almost quantitative yield of *trans*- $\gamma$ -hydroxy- $\beta\beta$ -dimethylpentamethylene- $\alpha$ -carboxylic acid (m. p.  $101^\circ$ ),

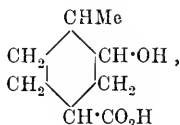


is obtained. The most remarkable property of this acid is its great stability\* since, although it is a  $\gamma$ -hydroxy-acid, it does not yield a lactone on boiling with dilute sulphuric acid and, even when distilled, it passes over for the most part unchanged.

This unusual stability, even of a *trans*-modification of a  $\gamma$ -hydroxy-acid, led us to suspect that some intramolecular change might have taken place during the energetic reduction with sodium and alcohol, but that this is not the case is proved by the behaviour of the hydroxy-acid on treatment with chromic acid, when it is very readily oxidised and converted into the  $\gamma$ -keto-acid from which it had been obtained by reduction.

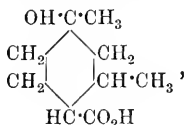
When *trans*- $\gamma$ -hydroxydimethylpentamethylenecarboxylic acid is heated with hydrobromic acid, it yields  $\gamma$ -bromodimethylpentamethylenecarboxylic acid, and this viscid, syrupy substance, when boiled with sodium carbonate, loses hydrogen bromide with the formation of dimethylcyclopentenecarboxylic acid (b. p.  $236^\circ$ ) :

\* The reason for the remarkable stability of this hydroxy-acid is difficult to understand, but it may be mentioned that other closed chain  $\gamma$ -hydroxy-acids are known—for example, the  $\gamma$ -hydroxyhexahydro-*p*-toluic acid :



prepared by Tiemann and Semmler (*Ber.*, 1895, **28**, 2143)—which also exhibit very little tendency to yield lactones (compare Perkin and Yates, *Trans.*, 1901, **79**, 1375).

On the other hand, *trans*-hydroxyhexahydro-xylic acid,



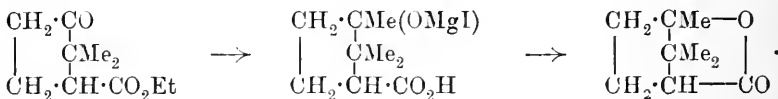
in which the hydroxy-group is in the  $\delta$ -position with respect to the carboxyl radicle, readily yields a lactone on distillation (Perkin and Lees, *Trans.*, 1901, **79**, 344), and this and other similar observations seem to point to the possibility of lactone formation taking place more readily in the  $\delta$ - than in the  $\gamma$ -position in ring compounds.



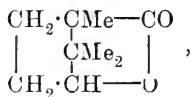
*Action of Magnesium Methyl Iodide on Ethyl Ketodimethylpentamethylenecarboxylate. Formation of  $\alpha$ -Campholactone and Synthesis of  $\alpha$ -Campholytic Acid and  $\beta$ -Campholytic Acid (isoLauronic Acid).*

As stated on p. 128, the primary object of this research was the synthesis of closed chain compounds closely allied to camphor and this was accomplished in the following way.

Ethyl ketodimethylpentamethylenecarboxylate is readily acted on by magnesium methyl iodide with the formation of several substances, among which is a new lactone produced according to the following scheme:



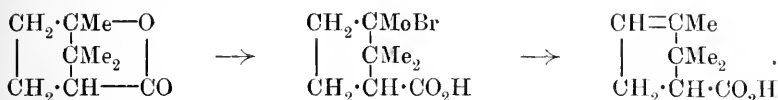
On account of its close relationship to campholactone,



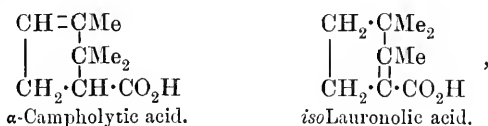
from which, indeed, it only differs in the reversal of the position of the lactone group, this new lactone has been named *inactive  $\alpha$ -campholactone*.\*

Inactive  $\alpha$ -campholactone is an oil which smells strongly of peppermint and distils at 155–157° under 50 mm. pressure; when treated with hydrobromic acid, it yields *inactive  $\gamma$ -bromotrimethylpentamethylenecarboxylic acid*, which melts at 108° and, when digested with sodium carbonate, loses hydrogen bromide with the formation of the corresponding unsaturated acid:

\* In the preliminary notice of this research in the *Proceedings* (*loc. cit.*), we named the new lactone "*isocampholactone*" in order to emphasise its great similarity to campholactone. We subsequently found, however, that this name had already been given to a lactone of unknown constitution which Noyes (*Ber.*, 1895, 28, 553) had prepared by the action of nitrous acid on aminolauronic acid. This latter lactone, which melts at 23° and has quite different properties to our synthetical lactone, was not obtained in sufficient quantity for analysis, but its method of formation makes it probable that it is isomeric (possibly stereoisomeric) with campholactone. Owing to the name "*isocampholactone*" having been previously used by Noyes, we have altered that of our lactone to " *$\alpha$ -campholactone*."



The formula of this unsaturated acid is that of *inactive α-campholytic acid*, an acid which was first obtained by one of us (Perkin, *Trans.*, 1903, 83, 853) by the reduction of *α*-camphylic acid,  $\text{C}_8\text{H}_{11} \cdot \text{CO}_2\text{H}$ , with sodium amalgam. In order to prove that the synthetical acid is *inactive α-campholytic acid*, it was digested with dilute sulphuric acid when crystals were formed which melted at  $132^\circ$  and were easily identified as *β-campholytic acid* (*isolauronic acid*), the well-known remarkable isomeric change indicated by the formulæ,



having taken place. That the *isolauronic acid* thus synthesised is identical with the acid obtained from camphoric acid was shown by mixing equal quantities of the two preparations when the mixture melted at  $132^\circ$ , the melting point of the constituents. Furthermore, the synthetical acid, on oxidation with permanganate, yielded *isolauronic acid*.

There can thus be no doubt that the above series of reactions constitutes a synthesis of both inactive *α*-campholytic acid and of *isolauronic acid* (*β*-campholytic acid) and therefore the constitution of these important acids may now be taken as definitely established.

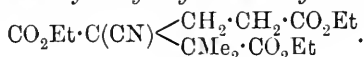
If the formulæ of *α*-campholactone and the derivatives obtained from it are carefully examined, it will be at once seen how very closely these synthetical substances are related to camphoric acid. Thus if *γ*-bromotrimethylpentamethylenecarboxylic acid be taken as an example, it is only necessary to replace the bromine atom in that substance by the carboxyl group in order to accomplish a synthesis of camphoric acid :



Many experiments were made, under the most varied conditions, in the hope of being able to bring about this change, but with little success. Thus the bromo-acid and its ester were treated with silver cyanide, with solid potassium cyanide, alone and in the presence of anhydrous hydrogen cyanide, and with aqueous and alcoholic solutions of potassium cyanide, but although small quantities of a crystalline sub-

stance having properties identical with those of *i*-camphoric acid were obtained in two cases (see p. 146), the amount was too small for analysis and definite identification. The cause of the failure in these experiments is the great readiness with which the bromo-acid loses hydrogen bromide with the formation of  $\alpha$ -campholytic acid. Again  $\alpha$ -campholactone was heated with potassium cyanide and with anhydrous formic acid, but in both cases,  $\alpha$ -campholytic acid was the product of the reaction. Lastly, a synthesis, similar to that of benzoic acid from bromobenzene by the action of magnesium powder and carbon dioxide, was attempted with the ester of bromotrimethylpentamethylene-carboxylic acid, but again without success. It has not been thought worth while to describe all these various experiments in detail in this paper, the above short account being sufficient to indicate the reactions which were attempted with the object of synthesising camphoric acid from  $\alpha$ -campholactone.

*Condensation of Ethyl Cyanodimethylsuccinate with Ethyl  $\beta$ -Iodopropionate. Formation of Ethyl Cyanodimethylbutanetricarboxylate,*



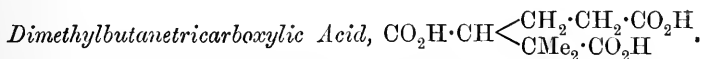
In carrying out this condensation, it was found that even slight differences in temperature and other conditions had a very marked influence on the yield of the condensation product, and the best results were usually obtained by working in the following way. Sodium (23 grams) is dissolved in absolute alcohol (350 c.c.) and, after cooling thoroughly, mixed with ethyl cyanodimethylsuccinate (227 grams) and then ethyl  $\beta$ -iodopropionate (228 grams) added in small quantities, care being taken, by cooling with water, that the temperature never rises above 25°. After 12 hours, the product is heated on the water-bath for 2 hours, water is then added, and the oily ester, which smells strongly of ethyl acrylate, is twice extracted with ether. The ethereal solution is thoroughly washed with water, dried over calcium chloride, and the ether very slowly distilled off; the residual oil is then distilled at first under the ordinary pressure until the temperature rises to 130° in order that the ethyl acrylate which comes over below this may be collected for subsequent use (see p. 136).

The distillation flask is then attached to the vacuum apparatus and the distillation continued under 20 mm. pressure when, after several fractionations, *ethyl cyanodimethylbutanetricarboxylate* is readily obtained pure as a colourless oil boiling at about 210° (20 mm.).

0.2976 gave 11.3 c.c. of nitrogen at 23° and 760 mm.  $N = 4.3$ .

$\text{C}_{16}\text{H}_{25}\text{O}_6\text{N}$  requires  $N = 4.3$  per cent.

The yield of this ester varies in a remarkable way in different experiments carried out, apparently, under precisely the same conditions. In one instance, an almost theoretical yield was obtained, but in other cases hardly a trace was produced, the average yield being about 25 per cent. of the theoretical. The remainder consists of ethyl acrylate and unchanged ethyl cyanodimethylsuccinate and sometimes a considerable quantity of an oil having a high boiling point is produced.



The cyanogen group in ethyl cyanodimethylbutanetricarboxylate is hydrolysed only with great difficulty, even on long boiling with hydrochloric or dilute sulphuric acid the process is far from complete, and it was only by employing concentrated sulphuric acid in the first instance that a satisfactory result was ultimately obtained. The cyano-ester (in quantities of 50 grams) is dissolved in an equal volume of concentrated sulphuric acid, and, when the solution is cold, water is added until oily drops just commence to separate. The whole is then boiled on the sand-bath, the alcohol produced being allowed to escape through the air-condenser, and small quantities of water are added from time to time in order to prevent charring. After 8 hours, the solution is diluted with an equal volume of water, saturated with ammonium sulphate, and extracted several times with ether; the solvent is then evaporated and the residue dissolved in a small quantity of water and mixed with an equal volume of concentrated hydrochloric acid. After two days, the crystalline crust which has separated is collected and purified by recrystallisation from hydrochloric acid, from which it separates as a sandy powder.

0.1444 gave 0.2615  $\text{CO}_2$  and 0.0860  $\text{H}_2\text{O}$ . C = 49.4; H = 6.6.

0.1298 „ 0.2359  $\text{CO}_2$  „ 0.0750  $\text{H}_2\text{O}$ . C = 49.5; H = 6.4.

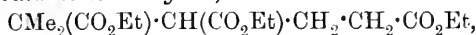
$\text{C}_9\text{H}_{14}\text{O}_6$  requires C = 49.5; H = 6.4 per cent.

*Dimethylbutanetricarboxylic acid* melts at 155—157° and is readily soluble in water, but sparingly so in concentrated hydrochloric acid. It is rather sparingly soluble in dry ether, and crystallises from this solvent in small, glistening prisms or leaflets.

On titration with decinormal caustic soda, 0.2018 gram neutralised 0.1108 gram of NaOH, whereas this quantity of a tribasic acid,  $\text{C}_9\text{H}_{14}\text{O}_6$ , should neutralise 0.1110 gram of NaOH.

The hydrochloric acid mother liquors from the purification of the acid contain a large quantity of very impure material; this is extracted with ether, and, after evaporating off the solvent, the residue is esterified by boiling with alcohol and sulphuric acid. The ester is extracted

in the usual way and fractionated under reduced pressure, when pure *ethyl dimethylbutanetricarboxylate*,



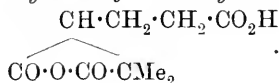
is obtained as a colourless oil boiling at about  $195^\circ$  (40 mm.).

0.1722 gave 0.3761  $\text{CO}_2$  and 0.1319  $\text{H}_2\text{O}$ .  $\text{C} = 59.5$  ;  $\text{H} = 8.5$ .

$\text{C}_{15}\text{H}_{26}\text{O}_6$  requires  $\text{C} = 59.6$  ;  $\text{H} = 8.6$  per cent.

From this ester, the pure tribasic acid is readily obtained by hydrolysis with concentrated hydrochloric acid.

*The Internal Anhydride of Dimethylbutanetricarboxylic Acid,*



When dimethylbutanetricarboxylic acid is heated under reduced pressure (45 mm.), it melts and then, at once, gives off water, and the anhydro-acid distils at about  $255^\circ$  as a viscid, colourless syrup which soon begins to crystallise in stellate groups and gradually becomes solid. By dissolving in hot benzene and allowing to cool slowly, the substance is obtained in well-defined, four-sided plates, but if the solution is rapidly stirred, it separates as a sandy, crystalline precipitate.

0.1776 gave 0.3503  $\text{CO}_2$  and 0.0959  $\text{H}_2\text{O}$ .  $\text{C} = 53.8$  ;  $\text{H} = 6.0$ .

$\text{C}_9\text{H}_{12}\text{O}_5$  requires  $\text{C} = 54.0$  ;  $\text{H} = 6.0$  per cent.

The anhydride melts at  $98^\circ$  and is sparingly soluble in cold water ; it dissolves, however, readily on boiling with water, and if an equal volume of hydrochloric acid is added to the concentrated solution, crystals separate which melt at  $155$ — $157^\circ$  and consist of the pure tribasic acid.

*Formation of Ethyl Cyanodimethylbutanetricarboxylate from Ethyl Acrylate, Ethyl Cyanoacetate, and Ethyl Bromoisobutyrate.*

The reasons which led to this method being carefully worked out are given in the introduction. Sodium (23 grams) was dissolved in 300 grams of alcohol, mixed with ethyl cyanoacetate (113 grams), and, after well cooling, ethyl acrylate (100 grams) added in several portions. The condensation takes place very rapidly and with evolution of a considerable amount of heat, and in a short time the whole of the sodium compound of the ethyl cyanoacetate will have passed into solution. The mixture is heated on the water-bath for about two hours, and until a drop of the liquid, on dilution with water, no

longer deposits an oil ; it is then mixed with ethyl bromoisobutyrate (195 grams) and heated in soda-water bottles in a boiling salt-bath for eight hours. On diluting with water, extracting the oily product with ether, and fractionating under reduced pressure, pure ethyl cyanodimethylbutanetricarboxylate is obtained, the yield being 75—80 per cent. of the theoretical.

0.2646 gave 10.2 c.c. of nitrogen at 20° and 755 mm.  $N = 4.4$ .

$C_{16}H_{25}O_6N$  requires  $N = 4.3$  per cent.

That this cyano-ester has the same constitution as that obtained by the process described on p. 134 was proved by hydrolysis with sulphuric acid, when a good yield of dimethylbutanetricarboxylic acid was obtained which melted at 155—157°.

0.1516 gave 0.2759  $CO_2$  and 0.0886  $H_2O$ .  $C = 49.6$  ;  $H = 6.5$ .

$C_9H_{14}O_6$  requires  $C = 49.5$  ;  $H = 6.4$  per cent.

Much of the acid required for this investigation was prepared by the foregoing process.

#### *Partial Hydrolysis of Ethyl Cyanodimethylbutanetricarboxylate.*

During the course of this investigation, a number of experiments were instituted with the object of eliminating the carboxyl radicle adjacent to the cyanogen group in ethyl cyanodimethylbutanetricarboxylate, and the results obtained may be briefly described as follows.

When an alcoholic solution of 12 grams of pure caustic potash is mixed with 35 grams of the cyano-ester and the whole allowed to remain overnight, a crystalline potassium salt separates in quantity. This was collected at the pump, washed with alcohol, in which it is sparingly soluble, and dried at 100° ; it then weighed 10 grams.

0.3484 gave 0.1781  $K_2SO_4$ .  $K = 22.9$ .

$C_{12}H_{15}O_6NK_2$  requires  $K = 22.4$  per cent.

The constitution of this salt is probably represented by the formula

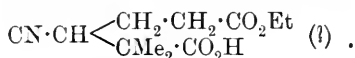


It was very soluble in water and gave no precipitate on acidifying with hydrochloric acid ; the whole was therefore repeatedly extracted with ether, the ethereal solution dried over calcium chloride and evaporated, when a colourless oil was obtained, which, over sulphuric acid in a vacuum desiccator, became very viscid but did not crystallise. The analysis shows that this substance is *ethyl dihydrogen cyanodimethylbutanetricarboxylate*, corresponding with the above potassium salt.

0.1974 gave 8.3 c.c. of nitrogen at 17° and 759 mm.  $N = 4.9$ .

$C_{12}H_{17}O_6N$  requires  $N = 5.2$  per cent.

When this dibasic acid is heated at 150°, it decomposes with evolution of carbon dioxide, and, when the evolution of gas has ceased, the residue distils almost completely at 245—250° (50 mm.) as a viscid oil which consists of *ethyl hydrogen cyanodimethylbutanedicarboxylate*,



0.2138 gave 11.5 c.c. of nitrogen at 20° and 759 mm.  $N = 6.2$ .

$C_{11}H_{17}O_4N$  requires  $N = 6.2$  per cent.

*Ketodimethylpentamethylenecarboxylic Acid*,  $CO_2H \cdot CH < \begin{matrix} CH_2 - CH_2 \\ CMe_2 \cdot CO \end{matrix}$ .

This acid is formed when the sodium salt of dimethylbutanetricarboxylic acid is heated with acetic anhydride. The sodium salt is prepared by dissolving the pure acid (109 grams) in water, adding 80 grams of anhydrous sodium carbonate, and evaporating the alkaline liquid to dryness. In order to obtain the salt as finely divided as possible, it is powdered and passed through a fine wire sieve, being then again dried at 100° and transferred to a flask, into the neck of which is fitted a tube bent twice at right angles. After adding 150 grams of freshly distilled acetic anhydride, the whole is slowly heated in an oil-bath when it will be noticed that carbon dioxide begins to come off below 100°, as can be readily seen by causing the tube attached to the flask to dip under baryta water. The temperature is kept at 135—140° for about 6 hours, then 50 grams of acetic anhydride are added and the heating continued until the evolution of carbon dioxide has practically ceased, which is the case after about three hours. As soon as the product is cold, it is esterified by adding an excess of a solution of one volume of sulphuric acid in three volumes of alcohol and heating for 6 hours on the water-bath in an open flask in order that as much ethyl acetate as possible may be removed by evaporation. The product, which smells strongly of ethyl acetate, is diluted with water and extracted several times with ether; the ethereal solution is then thoroughly washed with water and dilute sodium carbonate solution\* and evaporated.

On fractionating this oil under 100 mm. pressure, about 50 grams distil at 160—180° leaving a viscid, nearly black residue† in the retort

\* The dark sodium carbonate extract, on acidifying and extracting with ether, yields a brown oil from which considerable quantities of ketodimethylpentamethylenecarboxylic acid may be obtained by treatment with semicarbazide or by esterification and distillation under reduced pressure and subsequent hydrolysis.

† The residues from several preparations were mixed and fractionated under

and, on repeatedly fractionating the distillate, an oil (35 grams) is obtained which boils at  $170\text{--}172^\circ$  (100 mm.) and consists of pure *ethyl ketodimethylpentamethylenecarboxylate*.

0.1765 gave 0.4196  $\text{CO}_2$  and 0.1397  $\text{H}_2\text{O}$ . C = 64.8; H = 8.8.

0.1584 „ 0.3771  $\text{CO}_2$  „ 0.1242  $\text{H}_2\text{O}$ . C = 64.9; H = 8.7.

$\text{C}_{10}\text{H}_{16}\text{O}_3$  requires C = 65.2; H = 8.7 per cent.

This ester is hydrolysed by boiling with an excess of methyl-alcoholic potash; the solution is diluted with water, neutralised, and evaporated until free from alcohol. After acidifying with hydrochloric acid and extracting six times with pure ether, the ethereal solution is dried over calcium chloride and evaporated, when a pale yellow oil is obtained which, on cooling, rapidly solidifies. The mass is left in contact with porous porcelain to remove a trace of oily impurity, and then dissolved in a small amount of water, from which the pure acid separates slowly in groups of colourless needles.

0.1485 gave 0.3360  $\text{CO}_2$  and 0.1043  $\text{H}_2\text{O}$ . C = 61.6; H = 7.8.

0.1634 „ 0.3686  $\text{CO}_2$  „ 0.1144  $\text{H}_2\text{O}$ . C = 61.5; H = 7.8.

$\text{C}_8\text{H}_{12}\text{O}_3$  requires C = 61.5; H = 7.7 per cent.

*Ketodimethylpentamethylenecarboxylic acid* melts at  $109\text{--}110^\circ$ ; it dissolves readily in benzene, acetone, ether, alcohol, and chloroform, but is sparingly soluble in light petroleum. It is exceedingly soluble in hot water but much less so in the cold, and it may be obtained in long, colourless needles if the hot solution is allowed to cool very slowly. The pure acid also crystallises readily from ether in the form of hard, glistening prisms.

A slightly alkaline solution of the ammonium salt of the acid gives no precipitate with barium or calcium chloride, even on boiling; with copper sulphate, no precipitate is formed in the cold, but, on boiling, a pale blue, apparently crystalline, copper salt separates.

The *oxime*,  $\text{C}_6\text{H}_{11}(\text{C:N}\cdot\text{OH})\cdot\text{CO}_2\text{H}$ , was prepared by dissolving the acid in a considerable excess of caustic potash solution, adding twice the calculated quantity of hydroxylamine hydrochloride, and allowing the whole to remain for two days. On acidifying with hydrochloric acid, a crystalline precipitate separated, which was extracted with ether, the ethereal solution was carefully dried with calcium chloride and evaporated to a small bulk, when the oxime soon began to separate in crystalline crusts.

30 mm. pressure, when about one-third distilled at  $180\text{--}190^\circ$ . This portion, on hydrolysis with hydrochloric acid, yielded a considerable quantity of crude dimethylbutanetricarboxylic acid, which was purified by recrystallisation, first from hydrochloric acid and then from ether.

0.203 gave 15.3 c.c. nitrogen at 19° and 737 mm.  $N = 8.3$ .

$C_8H_{13}O_3N$  requires  $N = 8.2$  per cent.

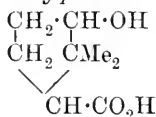
*Ketoximedimethylpentamethylenecarboxylic acid* melts at about 195°, but it turns brown and commences to decompose below this temperature. It is somewhat sparingly soluble even in boiling water, and separates, on cooling, as a sandy powder. It dissolves readily in sodium carbonate, and, when heated in a test-tube, it decomposes with a slight explosion, and yields an oily distillate which crystallises on cooling.

The *semicarbazone*,  $C_6H_{11}(C:N \cdot NH \cdot CO \cdot NH_2) \cdot CO_2H$ , separates at once as a sandy powder when a concentrated aqueous solution of the acid is mixed with semicarbazide hydrochloride and sodium acetate. It melts at about 217° and is very sparingly soluble in water.

0.1544 gave 26.6 c.c. nitrogen at 19° and 751 mm.  $N = 19.5$ .

$C_9H_{15}O_3N_3$  requires  $N = 19.7$  per cent.

*Reduction of Ketodimethylpentamethylenecarboxylic Acid. Formation of trans-γ-Hydroxydimethylpentamethylenecarboxylic Acid,*



It is stated in the introduction that ketodimethylpentamethylenecarboxylic acid is not reduced by sodium amalgam, and this was shown by the fact that when 30 grams of the acid, dissolved in dilute aqueous caustic soda, was boiled with 2500 grams of 4 per cent. sodium amalgam, and the solution subsequently acidified and extracted with ether, almost the whole of the keto-acid was recovered unchanged. When, however, the boiling alcoholic solution of the acid is treated with sodium, reduction is readily effected. The pure acid (30 grams) was dissolved in about 500 c.c. of absolute alcohol, heated to boiling in a reflux apparatus, and treated, as rapidly as possible, with 70 grams of sodium, boiling alcohol being added from time to time as the reaction slackened. The product was dissolved in much water, evaporated on the water-bath until free from alcohol, acidified with an excess of hydrochloric acid, and heated on the water-bath for half an hour in the expectation that the hydroxy-acid, if present, would thus be converted into its lactone. As, however, no neutral oil separated, the whole was saturated with ammonium sulphate, and extracted 10 times with ether. The ethereal solution was dried over calcium chloride and evaporated, when 28 grams of a viscid oil remained and solidified on cooling. That no unchanged keto-acid was present in this product was shown by treating a small portion with semicarbazide and sodium

acetate, when no trace of the very sparingly soluble semicarbazone (p. 140) was formed. Considerable difficulty was experienced in recrystallising the crude reduced acid, but this was ultimately accomplished by dissolving it in dry ether, adding an equal volume of benzene, and allowing the solution to evaporate slowly at the ordinary temperature. The crystalline crusts thus obtained were drained on porous porcelain, and dissolved in a small quantity of hot water, when, on slowly cooling, the pure acid separated in well-defined, glistening prisms.

0.1690 gave 0.3762  $\text{CO}_2$  and 0.1326  $\text{H}_2\text{O}$ .  $\text{C} = 60.7$ ;  $\text{H} = 8.7$ .

0.1353 „ 0.3012  $\text{CO}_2$  „ 0.1075  $\text{H}_2\text{O}$ .  $\text{C} = 60.7$ ;  $\text{H} = 8.8$ .

$\text{C}_8\text{H}_{14}\text{O}_3$  requires  $\text{C} = 60.8$ ;  $\text{H} = 8.8$  per cent.

*trans*- $\gamma$ -Hydroxydimethylpentamethylenecarboxylic acid melts at  $100$ – $101^\circ$  and is readily soluble in water, alcohol, and ether. That it is a monobasic acid was shown by its behaviour with decinormal caustic soda, when 0.1977 gram of the acid required for neutralisation 0.0507 gram of  $\text{NaOH}$ , whereas this amount of a monobasic acid,  $\text{C}_8\text{H}_{14}\text{O}_3$ , should neutralise 0.0506 gram of  $\text{NaOH}$ .

This  $\gamma$ -hydroxy-acid is remarkably stable, and shows no tendency to become converted into a lactone when boiled with dilute hydrochloric or sulphuric acid, and, even on distillation, it does not yield a lactone, as is proved by the following experiment.

Three grams of the pure acid were distilled under 40 mm. pressure, when the whole passed over at  $205$ – $210^\circ$  as a viscid, colourless oil resembling glycerol, and this, on cooling, solidified to a brittle, transparent, glassy mass. This product was completely soluble in cold dilute sodium carbonate solution, showing that it was not a lactone, and, without further purification, it yielded numbers which differ little from those required by the hydroxy-acid.

0.1649 gave 0.3718  $\text{CO}_2$  and 0.1348  $\text{H}_2\text{O}$ .  $\text{C} = 61.4$ ;  $\text{H} = 9.0$ .

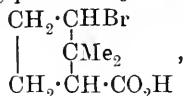
$\text{C}_8\text{H}_{14}\text{O}_3$  requires  $\text{C} = 60.8$ ;  $\text{H} = 8.8$  per cent.

*Oxidation by Means of Chromic Acid.*—Owing to the curious properties of this hydroxy-acid, it was thought necessary to investigate its behaviour on oxidation in order to prove that its constitution is that represented by the formula indicated on p. 140. The pure acid (2 grams) was dissolved in water, mixed with potassium dichromate (1.4 grams) and a small amount of sulphuric acid, and gradually heated to boiling when oxidation readily took place. The product was extracted with ether, the ethereal solution dried over calcium chloride and evaporated to a small bulk, when crystalline crusts (1.5 grams) slowly separated, which melted at  $109^\circ$ , and consisted of pure ketodimethylpentamethylenecarboxylic acid.

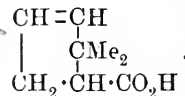
0.1558 gave 0.3513  $\text{CO}_2$  and 0.1096  $\text{H}_2\text{O}$ .  $\text{C} = 61.5$ ;  $\text{H} = 7.8$ .

$\text{C}_8\text{H}_{12}\text{O}_3$  requires  $\text{C} = 61.5$ ;  $\text{H} = 7.7$  per cent.

*$\gamma$ -Bromodimethylpentamethylenecarboxylic Acid,*



*and Dimethylcyclopentenecarboxylic Acid,*



Finely powdered  $\gamma$ -hydroxydimethylpentamethylenecarboxylic acid dissolves readily in fuming hydrobromic acid (saturated at  $0^\circ$ ), but the bromo-acid does not separate after a time as is the case with the corresponding trimethyl acid (see p. 145). The solution was therefore heated in a sealed tube at  $100^\circ$  for about fifteen minutes, when, on cooling, an oily layer had separated on the surface of the hydrobromic acid. The whole was diluted with water, extracted with ether, the ethereal solution thoroughly washed with water, dried over calcium chloride, and evaporated, when an almost colourless oil remained which, after leaving for some hours over sulphuric acid in a vacuum desiccator, was analysed with the following result :

0.3373 gave 0.2346  $\text{AgBr}$ .  $\text{Br} = 35.9$ .

$\text{C}_8\text{H}_{13}\text{O}_3\text{Br}$  requires  $\text{Br} = 36.2$  per cent.

*$\gamma$ -Bromodimethylpentamethylenecarboxylic acid*, when prepared in this way, shows no signs of crystallising, even when left for a long time in a freezing mixture, and, on exposure to the air, it becomes darker and finally almost black. A quantity of the freshly prepared bromo-acid was dissolved in excess of sodium carbonate and boiled for several minutes; the solution was then acidified and extracted with ether. After drying over calcium chloride and evaporating, an oil was obtained which distilled for the most part at  $160$ — $170^\circ$  (50 mm.), but there was a considerable quantity of a viscid oil left in the flask, which probably consisted of regenerated  $\gamma$ -hydroxy-acid. The distillate was fractionated under the ordinary pressure, when almost the whole passed over at  $236^\circ$  (760 mm.) as an oil which was colourless when hot but became deep sage-green on cooling, a behaviour often observed in connection with substances belonging to the camphor and terpene series.

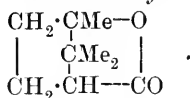
Owing to its method of formation, there can be no doubt that the oily acid thus obtained is *dimethylcyclopentenecarboxylic acid*. That it is an unsaturated acid is shown by the fact that its solution in sodium carbonate instantly decolorises permanganate.

0.2128 gave 0.5315  $\text{CO}_2$  and 0.1638  $\text{H}_2\text{O}$ . C = 68.2 ; H = 8.5.

0.1730 „ 0.4336  $\text{CO}_2$  „ 0.1335  $\text{H}_2\text{O}$ . C = 68.3 ; H = 8.6.

$\text{C}_8\text{H}_{12}\text{O}_2$  requires C = 68.6 ; H = 8.6 per cent.

*The Action of Magnesium Methyl Iodide on Ethyl Ketodimethylpentamethylenecarboxylate. Formation of Inactive  $\alpha$ -Campholactone.*



After a long series of comparative experiments, the following process was ultimately adopted for the preparation of  $\alpha$ -campholactone. Finely-divided magnesium filings (7.2 grams) are placed in a 2 litre flask connected with a long water condenser and covered with ether (300 c.c.) which had been very carefully freed from water, and finally distilled over phosphoric oxide. Methyl iodide (45 grams) is then added in two portions, the vigorous reaction being kept under control by immersing the flask in ice water occasionally.

Ethyl ketodimethylpentamethylenecarboxylate (37 grams) is dissolved in pure ether (300 c.c.) in a large flask, connected with a reflux condenser, and immersed in powdered ice and water ; the ethereal solution of magnesium methyl iodide is then cautiously poured down the condenser tube in several small quantities, the flask being well agitated and allowed to cool thoroughly after each addition. As each quantity of the magnesium methyl iodide comes into contact with the ethereal solution of the keto-ester, a yellowish-white turbidity is produced, and ultimately the magnesium compound separates on the sides of the flask as a sticky mass. After half an hour, the product is decomposed by the careful addition of dilute hydrochloric acid, the yellow ethereal solution is separated, washed with dilute hydrochloric acid and evaporated, and the residue, which is a mixture of the lactone, unchanged keto-ester, and a neutral substance (which has not yet been investigated), is treated as follows. The deep yellow oil is dissolved in methyl alcohol, and digested for 10 minutes with a solution of caustic potash (20 grams) in methyl alcohol, by which means the lactone and keto-ester are hydrolysed ; water is then added, and the neutral substance removed by extraction with ether. The aqueous solution is evaporated on the water-bath until free from ether and methyl alcohol ; it is then diluted with water and acidified, when a viscid oil separates, which, on heating on the water-bath for 15 minutes, becomes limpid, owing to the conversion of the hydroxy-acid into the corresponding lactone. The whole is extracted with ether, the ethereal solution repeatedly washed with dilute aqueous sodium carbonate, dried over calcium chloride, and evaporated, when an oil

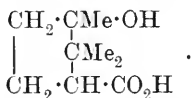
(6—8 grams) is obtained which, after repeated fractionation, distils constantly at 155—157° (50 mm.), and consists of pure *inactive*  $\alpha$ -campholactone.

0.1649 gave 0.4227 CO<sub>2</sub> and 0.1392 H<sub>2</sub>O. C = 69.9; H = 9.3.

0.1485 „ 0.3819 CO<sub>2</sub> „ 0.1238 H<sub>2</sub>O. C = 70.0; H = 9.2.

C<sub>9</sub>H<sub>14</sub>O<sub>2</sub> requires C = 70.1; H = 9.1 per cent.

Inactive  $\alpha$ -campholactone is a pale yellow oil which has a most pungent odour of peppermint; it is readily volatile in steam, and distils under the ordinary pressure almost without decomposition. It is insoluble in sodium carbonate solution, but dissolves readily and completely in warm dilute aqueous caustic soda, and the well-cooled solution, on acidifying, remains clear for a considerable time, indicating that the hydroxy-acid corresponding with the lactone is present; this acid is slowly decomposed at the ordinary temperature, and more rapidly on warming, with a separation of the lactone. A special experiment was made in the hope of being able to obtain the hydroxy-acid in a crystalline condition, in order that a direct comparison might be made with the hydroxydihydrocampholytic acid described by Noyes\* (*Amer. Chem. J.*, 1894, 16, 307, 502; 1896, 18, 685), and which he considers has the same constitution, namely,



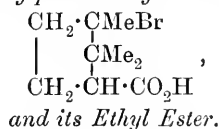
The pure lactone (2 grams) was dissolved in hot baryta water, the solution cooled with ice, acidified, and extracted with ether. On removing the ether by a current of dry air, a viscid oil remained, which was obviously the hydroxy-acid, since it dissolved readily and completely in dilute sodium carbonate solution.

0.1496 gave 0.3454 CO<sub>2</sub> and 0.1252 H<sub>2</sub>O. C = 64.0; H = 9.3.

C<sub>9</sub>H<sub>16</sub>O<sub>3</sub> requires C = 62.8; H = 9.3 per cent.

*Inactive*  $\gamma$ -cis-hydroxytrimethylpentamethylenecarboxylic acid, when left over sulphuric acid in a vacuum desiccator, rapidly loses water with the formation of  $\alpha$ -campholactone and, when boiled with hydrochloric acid, the change is complete in a few minutes. Hydroxydihydrocampholytic acid, on the contrary, is perfectly stable and, indeed, does not shew any tendency to yield a lactone even when boiled with acids; if then it has the constitution represented above, it must obviously be the *trans*-modification.

\* Compare Meyer and Jackson (*Lehrbuch der Org. Chem.*, Vol. II, 1021).

*Inactive  $\gamma$ -Bromotrimethylpentamethylenecarboxylic Acid,*

When  $\alpha$ -campholactone is mixed with three times its volume of fuming hydrobromic acid (saturated at  $0^\circ$ ) it dissolves, but almost immediately the liquid clouds and a viscid oil separates on the surface of the acid. This oily layer soon darkens in colour and crystallises, and in preparing the pure bromo-acid it is best to stir vigorously with a glass rod, so that solidification may be complete before decomposition sets in. The solid is thoroughly washed with water to remove hydrobromic acid and spread on porous porcelain to separate the oily impurity. The residue, which should be almost colourless, is made into a paste with a small quantity of formic acid (sp. gr. 1.22) and again transferred to porous porcelain, and after the operation has been repeated, a colourless, crystalline mass is obtained which softens at  $105^\circ$  and melts at about  $108^\circ$  with decomposition.

0.2202 gave 0.1735 AgBr. Br = 33.5.

$\text{C}_9\text{H}_{15}\text{O}_2\text{Br}$  requires Br = 34.0 per cent.

Inactive  $\gamma$ -bromotrimethylpentamethylenecarboxylic acid readily decomposes with loss of hydrogen bromide and formation of *inactive*  $\alpha$ -campholytic acid (see p. 147) and therefore no attempts were made to purify it by recrystallisation. As explained in the introduction, it is exactly similar in its chemical properties to the hydrobromide of  $\alpha$ -campholytic acid (*cistrans*-campholytic acid), which, according to Noyes (*Ber.*, 1898, 28, 551), melts at  $98$ — $100^\circ$  and decomposes in moist air, evolving hydrogen bromide.

The *ethyl* ester,  $\text{C}_9\text{H}_{14}\text{Br} \cdot \text{CO}_2\text{Et}$ .—In preparing this ester, the pure lactone (4 grams) was mixed with phosphorous pentabromide (15 grams), when a vigorous action took place and much hydrogen bromide was evolved. After 10 minutes, the whole was heated on the water-bath for 5 minutes and then poured, in a thin stream, into a large excess of absolute alcohol. As soon as the reaction had subsided, the solution was allowed to cool, diluted with water, and the heavy oil extracted with ether, the ethereal solution was washed with water and dilute sodium carbonate solution, dried over calcium chloride, evaporated, and the residual oil rapidly fractionated under 70 mm. pressure.

A small quantity of oil passed over below  $165^\circ$  and then almost

the whole of the remainder distilled at 165—170° leaving only a small, black residue in the flask.

0.1854 gave 0.1377 AgBr. Br = 31.6.

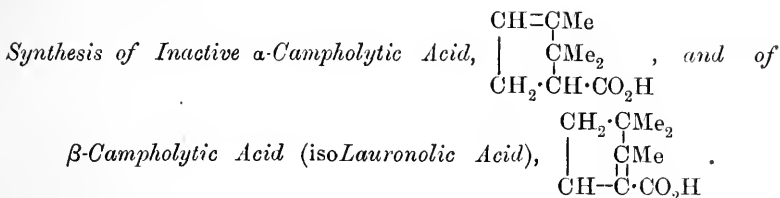
$C_{11}H_{19}O_2Br$  requires Br = 30.5 per cent.

This oil was made the starting-point in a long series of experiments instituted in the hope of synthesising camphoric acid (see p. 133) but without success. The above analysis and general properties of the oil leave, however, scarcely any doubt that it is *inactive ethyl  $\gamma$ -bromotrimethylpentamethylenecarboxylate*.

*Action of Potassium Cyanide on Bromotrimethylpentamethylenecarboxylic Acid.*—It was stated in the introduction that, in experimenting on the action of cyanides on this bromo-acid, an acid identical in properties with *i*-camphoric acid was obtained in very small quantities in two cases. In one instance, the experiment was carried out as follows: freshly prepared bromotrimethylpentamethylenecarboxylic acid (10 grams) was dissolved in alcohol, mixed with a concentrated aqueous solution of pure potassium cyanide (5 grams) and 5 c.c. of anhydrous hydrogen cyanide, the mixture being allowed to remain for 14 days. The dark brown product was heated on the water-bath for one hour, evaporated, and the residue mixed with concentrated hydrochloric acid and, after remaining overnight, heated for three hours on the water-bath. Water was then added and the whole distilled in steam until the distillate was free from  $\beta$ -campholytic acid (see p. 147). The residue was digested with animal charcoal, filtered, evaporated to a small bulk, and repeatedly extracted with ether, when a yellow oil was obtained which became semi-solid when left for some weeks over sulphuric acid.

This substance was drained on porous porcelain until all the oil had been absorbed and the residue recrystallised from a little water. As the crystalline product, which could not have weighed more than a few milligrams, melted indefinitely between 180° and 190°, it was heated in a test-tube with a small quantity of acetic anhydride when, on cooling, crystals separated which were drained on porous porcelain and washed with a little acetic anhydride. These crystals closely resembled the anhydride of *i*-camphoric acid, since they melted at 215—217° and gave on hydrolysis an acid, melting at 204°, whereas *i*-camphoric acid melts at 200—203° and yields an anhydride melting at 221°. Unfortunately, the amount at our disposal was quite insufficient to enable us to establish the identity of the substance by analysis.\*

\* The method of formation of this small quantity of acid and its properties leave scarcely room for doubt that it was *i*-camphoric acid, and experiments were in progress which it was hoped would have yielded enough material for definite



When  $\gamma$ -bromotrimethylpentamethylenecarboxylic acid is mixed with excess of sodium carbonate solution, it rapidly dissolves, and if the liquid is heated just to boiling, cooled, and acidified with hydrochloric acid, a viscid, oily layer of *inactive  $\alpha$ -campholytic acid* separates. This was extracted with ether, the ethereal solution washed until quite free from hydrochloric acid, dried over calcium chloride, evaporated, and the residual oil distilled under reduced pressure, when the whole passed over at  $162\text{--}164^\circ$  (45 mm.) as a colourless, viscid oil.

0.1441 gave 0.3696  $\text{CO}_2$  and 0.1185  $\text{H}_2\text{O}$ .  $\text{C} = 69.9$ ;  $\text{H} = 9.1$ .

$\text{C}_9\text{H}_{14}\text{O}_2$  requires  $\text{C} = 70.1$ ;  $\text{H} = 9.1$  per cent.

*Methyl  $\alpha$ -Campholytate*.—This ester was prepared by leaving the acid in contact with methyl alcohol and sulphuric acid for a short time and then precipitating with water. After extracting with ether, washing with sodium carbonate, drying over calcium chloride, and evaporating, an oil was obtained which distilled constantly at  $200^\circ$ .

0.1475 gave 0.3882  $\text{CO}_2$  and 0.1287  $\text{H}_2\text{O}$ .  $\text{C} = 71.7$ ;  $\text{H} = 9.7$ .

$\text{C}_8\text{H}_{13}\cdot\text{CO}_2\text{Me}$  requires  $\text{C} = 71.4$ ;  $\text{H} = 9.5$  per cent.

On hydrolysis with caustic potash and acidifying, this ester yielded liquid  $\alpha$ -campholytic acid, showing that no isomeric change had taken place during esterification (see below).

That the acid obtained in the way described above was inactive  $\alpha$ -campholytic acid and identical with the acid first obtained by the reduction of  $\alpha$ -camphylic acid with sodium amalgam (Trans., 1903, 83, 853) was proved by digesting a small quantity with 25 per cent. sulphuric acid for a few minutes, when, on cooling, a mass of crystals of  $\beta$ -campholytic acid (isolauronolic acid) separated.

These were collected, washed with water, and recrystallised from dilute acetic acid, when leaflets were obtained which melted at  $130^\circ$ .

0.1681 gave 0.4318  $\text{CO}_2$  and 0.1394  $\text{H}_2\text{O}$ .  $\text{C} = 70.0$ ;  $\text{H} = 9.1$ .

$\text{C}_9\text{H}_{14}\text{O}_2$  requires  $\text{C} = 70.1$ ;  $\text{H} = 9.1$  per cent.

identification. In the meantime, Komppa (*loc. cit.*) has published his brilliant synthesis of camphoric acid, which, once for all, establishes the correctness of Bredt's formula, and it is therefore quite unnecessary to investigate our much less satisfactory process any further.

The identity of this acid with the  $\beta$ -campholytic acid, obtained by the action of aluminium chloride on camphoric anhydride, was proved, firstly, by mixing equal quantities of the two acids, when no alteration in the melting point could be detected, and, secondly, by converting the synthetical acid into *isolauronic* acid by oxidation.

Two grams of the synthetical acid were dissolved in aqueous sodium carbonate, cooled with powdered ice, and then 2 per cent. potassium permanganate solution run in, drop by drop, until the pink colour just remained. The slight excess was destroyed by the addition of sodium sulphite, the whole was then heated to boiling and filtered, and the filtrate evaporated to a small bulk. The yellow liquid gave, on acidifying, a mass of pale yellow crystals which, after crystallising from water, melted at  $133^{\circ}$  and consisted of pure *isolauronic* acid.

0.1149 gave 0.2720  $\text{CO}_2$  and 0.0753  $\text{H}_2\text{O}$ .  $\text{C} = 64.5$ ;  $\text{H} = 7.3$ .

$\text{C}_9\text{H}_{12}\text{O}_3$  requires  $\text{C} = 64.3$ ;  $\text{H} = 7.1$  per cent.

Inactive  $\alpha$ -campholytic acid has been repeatedly obtained during the course of the experiments which have been carried out with  $\gamma$ -bromotrimethylpentamethylenecarboxylic acid and with  $\alpha$ -campholactone. Thus, for example, it is formed almost quantitatively when the bromo-acid is digested with potassium cyanide in alcoholic solution and when  $\alpha$ -campholactone is heated with dry potassium cyanide at  $110^{\circ}$ .

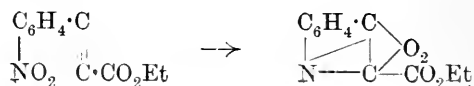
The authors wish to express their thanks to Mr. D. T. Jones for his valuable assistance in carrying out these experiments, and to state that much of the expense incurred during this investigation has been met by repeated grants from the Government Grant Fund of the Royal Society.

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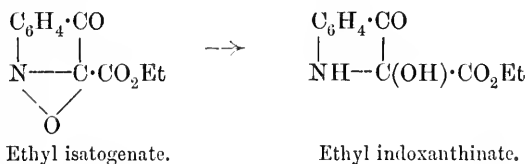
## XVI.—o-Nitrobenzoylacetic Acid.

By EDWARD RUSHTON NEEDHAM and WILLIAM HENRY PERKIN, jun.

IN the year 1881 (*Ber.*, 14, 1742), Baeyer showed that, when ethyl o-nitrophenylpropiolate is treated with sulphuric acid and the product poured into water, ethyl isatogenate is formed, and in explaining this remarkable process, he assumed that intramolecular change took place according to the scheme



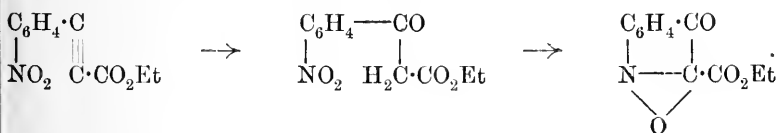
At a later date (*Ber.*, 1882, 15, 780) the same author, having discovered the reduction of ethyl isatogenate to ethyl indoxanthinate, explained this reaction by modifying the formula of the former ester and represented its relationship to the latter thus :



Subsequently he published a preliminary notice on benzoylactic acid (*Ber.*, 1882, 15, 2705) showing that its ethyl ester is produced when ethyl phenylpropiolate is dissolved in sulphuric acid and the product poured on to ice.

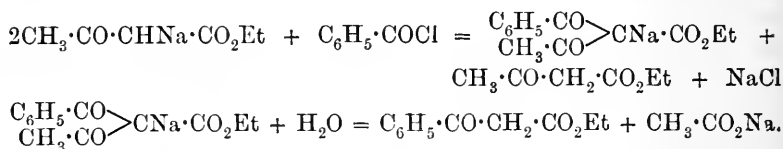
As far as we know, no explanation of the remarkable intramolecular change from ethyl *o*-nitrophenylpropiolate to ethyl isatogenate has ever been published, but the following series of changes has always appeared to one of us to be a possible explanation.

Just as ethyl phenylpropiolate when acted on by sulphuric acid takes up the elements of water yielding ethyl benzoylacetate, so in the case of ethyl *o*-nitrophenylpropiolate the first product of the reaction is probably ethyl *o*-nitrobenzoylacetate, which is then converted into ethyl isatogenate by an internal condensation brought about by the excess of sulphuric acid present :



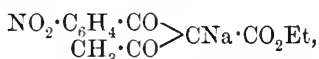
During the course of a long series of researches on ethyl benzoylacetate, carried out some years ago, many attempts were made to prepare ethyl *o*-nitrobenzoylacetate, not only with the object of testing the above view of the mechanism of the formation of ethyl isatogenate, but also on account of the close relationship which exists between ethyl *o*-nitrobenzoylacetate and many members of the indigo group. The attempts were, however, all unsuccessful at the time.

In 1896 (*Annalen*, 291, 67) Claisen described a very convenient method for preparing ethyl benzoylacetate, which consists in acting on two molecules of ethyl sodioacetoacetate with benzoyl chloride and then decomposing the sodium compound of ethyl benzoylacetate thus produced by boiling with ammonia and ammonium chloride :

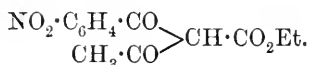


This process gives an excellent yield, and is not only much simpler than the preparation from ethyl phenylpropiolate and sulphuric acid, but is also to be preferred to the earlier method of Claisen and Lowman (*Ber.*, 1887, 20, 653) which consists in acting on a mixture of ethyl benzoate and ethyl acetate with sodium.

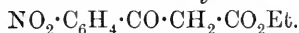
After experimenting with Claisen's process with very satisfactory results, we endeavoured to prepare ethyl *o*-nitrobenzoylacetate by a similar series of reactions, and were ultimately successful. When the ethyl sodioacetoacetate is treated with *o*-nitrobenzoyl chloride under the conditions described in the experimental part of this paper, the sodium compound of ethyl *o*-nitrobenzoylacetate,



is produced, and, when this is decomposed with hydrochloric acid, a red oil is obtained, which consists of nearly pure ethyl *o*-nitrobenzoylacetate,

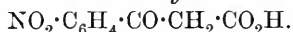


This substance is not new, but has already been prepared by Gevekoht (*Annalen*, 1883, 221, 323), who proved its constitution by showing that, when boiled with dilute sulphuric acid, it yields *o*-nitroacetophenone,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}_3$ . When the sodium compound of ethyl *o*-nitrobenzoylacetate is digested with ammonia and ammonium chloride, it is decomposed with the elimination of the acetyl group, and a red oil is produced which is crude *ethyl o*-nitrobenzoylacetate,



This is readily purified by conversion into the green, crystalline, copper compound,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CHCu}\cdot\text{CO}_2\text{Et}$ , and is thus obtained as a pale reddish-brown oil, which in its properties closely resembles ethyl benzoylacetate.

Experiments were next made on the action of concentrated sulphuric acid on ethyl *o*-nitrobenzoylacetate in the expectation that ethyl isatogenate would result, but we found, to our surprise, that the sulphuric acid had simply acted as a hydrolysing agent, and that the product of the action was *o*-nitrobenzoylactic acid,

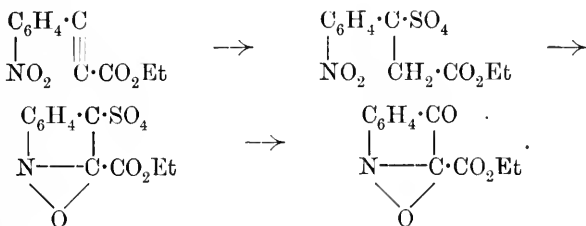


Even when the ester was heated with sulphuric acid at 90°, large

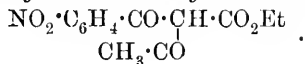
quantities of *o*-nitrobenzoylactic acid were formed, showing clearly that under these conditions there is no tendency for internal condensation to take place between the nitro-group and the methylene radicle.

The experiments described in this paper clearly prove that ethyl *o*-nitrobenzoylacetate is not an intermediate step in the conversion of ethyl *o*-nitrophenylpropiolate into ethyl isatogenate, and the problem of the mechanism of this remarkable reaction therefore remains unsolved.

In this conversion of ethyl *o*-nitrophenylpropiolate into ethyl isatogenate, it is possible that an additive compound with sulphuric acid may first be formed, this substance then undergoing internal condensation to yield a product, which, when decomposed with water, gives rise to ethyl isatogenate:



*Preparation of Ethyl o-Nitrobenzoylacetate,*



In preparing considerable quantities of this ester, we used a process based on the conditions recommended by Claisen (*Annalen*, 1896, 291, 67) for the preparation of ethyl benzoylacetate, and which differs in many respects from that described by Gevekoht (*Annalen*, 1883, 221, 323). *o*-Nitrobenzoic acid (100 grams) contained in a fractionating flask is gradually mixed with phosphorus pentachloride (135 grams), and as soon as the reaction, which commences in the cold, has slackened, the whole is heated on the water-bath until the crystals of the acid have entirely dissolved. The flask is then connected with the vacuum apparatus, and the phosphorus oxychloride distilled off at the lowest possible temperature. Sodium (31 grams) is now dissolved in 400 grams of absolute alcohol, and the solution made up to 500 c.c. by the addition of more alcohol. Pure ethyl acetoacetate (90 grams) is mixed with 250 c.c. of the sodium ethoxide solution, the whole cooled to 0°, and 56 grams of the *o*-nitrobenzoyl chloride added in small quantities at a time and with frequent shaking, care being taken that the temperature does not rise above 5°. After half an hour, 125 c.c. of the sodium ethoxide solution are added, and, after

thoroughly mixing, 28 grams of the acid chloride run in under the same conditions as before, then the whole is again left for half an hour and treated with the rest of the sodium ethoxide and *o*-nitrobenzoyl chloride. After remaining overnight at the ordinary temperature, the thick, yellow precipitate, which consists of the sodium compound of ethyl *o*-nitrobenzoylacetoacetate mixed with sodium chloride, is collected at the pump, and washed first with alcohol, and then with ether. It is then added to excess of dilute hydrochloric acid, cooled by the addition of powdered ice, and the whole shaken thoroughly with ether. The ethereal solution is washed with dilute aqueous sodium hydrogen carbonate, dried over calcium chloride, and evaporated, when a brownish-red oil is obtained which consists of nearly pure ethyl *o*-nitrobenzoylacetoacetate.

0.1696 gave 8.0 c.c. of nitrogen at 20° and 750 mm.  $N = 5.3$ .

$C_{13}H_{13}O_6N$  requires  $N = 5.0$  per cent.

Ethyl *o*-nitrobenzoylacetoacetate is a reddish-brown oil which gives a reddish-violet coloration when its solution in alcohol is mixed with ferric chloride. It dissolves in dilute aqueous caustic potash, and on adding a concentrated solution of this reagent a crystalline potassium compound,  $C_{13}H_{12}O_6NK$ , separates (compare Gevekoht, *loc. cit.*).

*Ethyl o-Nitrobenzoylacacetate*,  $NO_2 \cdot C_6H_4 \cdot CO \cdot CH_2 \cdot CO_2Et$ .

In the preparation of ethyl *o*-nitrobenzoylacacetate from ethyl *o*-nitrobenzoylacetoacetate, a method similar to that employed by Claisen (*loc. cit.*) in analogous cases, was adopted.

The crude sodium compound of ethyl *o*-nitrobenzoylacetoacetate, in quantities of 100 grams, was mixed with a solution of ammonium chloride (25 grams) in water (500 c.c.); 10 c.c. of concentrated aqueous ammonia, diluted with 90 c.c. of water, were then added, and the mass vigorously stirred with a turbine. As soon as the sodium compound had completely dissolved, the whole was mixed with powdered ice, acidified with hydrochloric acid, and at once extracted with ether. After washing with water, drying over anhydrous sodium sulphate and evaporating, crude ethyl *o*-nitrobenzoylacacetate remains as a brown oil, the yield being about 50 grams. This ester was purified in the following way. A solution of the blue cuprammonium compound, prepared by adding ammonia in slight excess to copper sulphate, was placed in a strong bottle, mixed with the crude ethyl *o*-nitrobenzoylacacetate dissolved in ten times its volume of ether, and vigorously shaken on the machine for 6 hours; the deep green copper compound, which had separated, was collected and washed, first with water and then with ether. After drying in a vacuum desiccator, the copper compound was

rapidly dissolved in excess of boiling toluene, from which it separates usually as a green powder, but if the crystallisation takes place very slowly and from dilute solutions, the substance is sometimes obtained in the form of definite violet crystals. When heated, this compound explodes with the formation of a thick, brown smoke, a behaviour which rendered its analysis very difficult. Ultimately the substance was first decomposed by gently warming with concentrated sulphuric acid, and, after driving off the excess of sulphuric acid, the residue was heated over the blowpipe, but, even in this way, a slight loss was unavoidable.

0.3050 gave 0.0406 CuO. Cu = 10.7.

0.4172 „ 0.0568 CuO. Cu = 11.0.

$\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CHCu} \frac{1}{2} \cdot \text{CO}_2\text{Et}$  requires Cu = 11.8 per cent.

In order to obtain pure ethyl *o*-nitrobenzoylacetate, the copper compound was ground to a fine paste with water, mixed with powdered ice, and decomposed by shaking with dilute hydrochloric acid and ether. The ethereal solution was washed thoroughly with water and dilute aqueous sodium hydrogen carbonate, dried over anhydrous sodium sulphate, evaporated, and the residual light brown oil left in a vacuum desiccator over sulphuric acid for two days.

0.1481 gave 0.3034  $\text{CO}_2$  and 0.0641  $\text{H}_2\text{O}$ . C = 55.8 ; H = 4.8.

0.2459 „ 12.2 c.c. of nitrogen at  $17^\circ$  and 754 mm. N = 5.9.

$\text{C}_{11}\text{H}_{11}\text{O}_5\text{N}$  requires C = 55.7 ; H = 4.6 ; N = 5.9 per cent.

*Ethyl o*-nitrobenzoylacetate has, so far, not been obtained in a crystalline condition ; when cooled to  $-10^\circ$ , it solidifies to a transparent resin which does not crystallise on rubbing. The alcoholic solution gives, with ferric chloride, an intense orange-red coloration which has a much yellower tint than that shown by either ethyl *p*- or *m*-nitrobenzoylacetate. It dissolves readily and completely in dilute caustic potash solution, forming an intense yellow solution, and is reprecipitated on the addition of acids, but if the yellow solution is mixed with concentrated aqueous caustic potash, a deep yellow, viscid oil separates, which when stirred vigorously, solidifies to a yellow cake of crystals, consisting of the *potassium* derivative of *ethyl o*-nitrobenzoylacetate,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CHK} \cdot \text{CO}_2\text{Et}$ . This product was drained on porous porcelain, rubbed up with a little water, and again transferred to porous porcelain, and after repeating this process, it was dried at  $100^\circ$  and analysed with the following result :

0.1450 gave 0.0466  $\text{K}_2\text{SO}_4$ . K = 14.4.

$\text{C}_{11}\text{H}_{10}\text{O}_5\text{NK}$  requires K = 14.2 per cent.

This potassium compound dissolves readily in water and when

acidified and extracted with ether, pure ethyl *o*-nitrobenzoylacetate is obtained as an almost colourless oil. When ethyl *o*-nitrobenzoylacetate is dissolved in dilute aqueous caustic soda and a strong solution of caustic soda added, the sodium compound is precipitated, but it is much more soluble than the potassium compound, and was not further investigated. Attempts were made to prepare the pure sodium compound by adding ether to the solution of the ester in the calculated quantity of sodium ethoxide, but no separation took place. If the same experiment is carried out with either ethyl *p*- or *m*-nitrobenzoylacetate, the sodium compound separates at once as a deep yellow, crystalline precipitate.

*o*-Nitrobenzoylactic acid,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ .

When ethyl *o*-nitrobenzoylacetate dissolves in concentrated sulphuric acid heat is generated, and the dark brown solution, when left for two or three days and then diluted with powdered ice, yields a brown solid which becomes almost colourless when drained on porous porcelain. The solid residue, which consists of almost pure *o*-nitrobenzoylactic acid, may be crystallised from water if the operation is rapidly carried out, but otherwise there is a great loss owing to decomposition into *o*-nitroacetophenone and carbon dioxide. The colourless needles thus obtained were dried over sulphuric acid and analysed with the following results:

0.1756 gave 0.3351  $\text{CO}_2$  and 0.0575  $\text{H}_2\text{O}$ .  $\text{C} = 52.0$ ;  $\text{H} = 3.4$ .

0.2274 „ 13.2 c.c. of nitrogen at  $16^\circ$  and 760 mm.  $\text{N} = 6.7$ .

$\text{C}_9\text{H}_7\text{O}_5\text{N}$  requires  $\text{C} = 51.7$ .  $\text{H} = 3.3$ ;  $\text{N} = 6.7$  per cent.

*o*-Nitrobenzoylactic acid melts at about  $117\text{--}120^\circ$  with vigorous decomposition, evidently yielding carbon dioxide and *o*-nitroacetophenone. It is readily soluble in alcohol and almost insoluble in cold, light petroleum; it dissolves moderately readily in warm benzene, and crystallises on cooling in colourless needles. The alcoholic solution of the pure acid gives a deep red coloration with ferric chloride. The composition of the acid was further controlled by titration, when it was found that 0.177 gram required for neutralisation 0.0335 gram of caustic soda, whereas this amount of a monobasic acid,  $\text{C}_9\text{H}_7\text{O}_5\text{N}$ , should neutralise 0.0339 gram of the alkali.

In order to study the decomposition products of *o*-nitrobenzoylactic acid, 3 grams of the pure acid were boiled with water, when a brisk effervescence took place, due to the evolution of carbon dioxide, and a heavy oil separated. This was extracted with ether, the ethereal solution washed with dilute aqueous sodium carbonate, dried over calcium chloride and evaporated, when an oil remained which was identified as *o*-nitroacetophenone.

0.1601 gave 11.9 c.c. of nitrogen at 15° and 745 mm.  $N = 8.4$ .

$C_8H_7O_3N$  requires  $N = 8.5$  per cent.

Five grams of pure ethyl *o*-nitrobenzoylacetate were dissolved in 20 c.c. of concentrated sulphuric acid and heated in a water-bath at 90° for 10 minutes. On cooling and diluting with ice, a solid soon separated which consisted of nearly pure *o*-nitrobenzoylacetic acid, and was finally purified in the manner already described.

0.2251 gave 13.1 c.c. of nitrogen at 15° and 750 mm.  $N = 6.8$ .

$C_9H_7O_5N$  requires  $N = 6.7$  per cent.

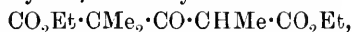
This experiment shows that the ethyl ester when heated with concentrated sulphuric acid is simply hydrolysed without undergoing any internal condensation.

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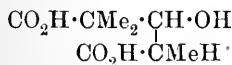
## XVII.—*The cis- and trans-Modifications of ααγ-Tri-methylglutaconic Acid.*

By WILLIAM HENRY PERKIN, jun., and ALICE EMILY SMITH, B.Sc.,  
1851 Exhibition Scholar of University College, Bangor.

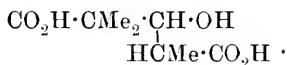
IN a recently published paper (Trans., 1903, 83, 772), it was shown that when ethyl *ααγ*-trimethylacetonedicarboxylate,



is reduced with sodium amalgam, it is converted into a mixture of the stereoisomeric modifications of *β*-hydroxy-*ααγ*-trimethylglutaric acid,

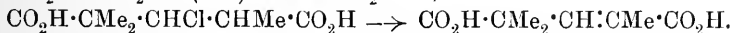


*Cis*, m. p. 115°.



*Trans*, m. p. 155°.

Both the *cis*- and *trans*-acids, when treated successively with phosphorus pentachloride and diethylaniline, yield *trans-ααγ*-trimethylglutaconic acid, which melts at 150°:



The *trans*-hydroxy-acid, when rapidly heated in small quantities, distils without decomposition, whereas the *cis*-hydroxy-acid is readily decomposed on distillation, forming an oily acid (see below) and a neutral crystalline substance,  $C_8H_{10}O_3$  (m. p. 88°), and it was suggested

that this latter is probably the anhydride of the *cis*-modification of  $\alpha\gamma$ -trimethylglutaconic acid:



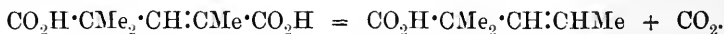
We have continued the investigation, and find that this view of the constitution of the substance  $\text{C}_8\text{H}_{10}\text{O}_3$  is correct. It is insoluble in aqueous sodium carbonate, but dissolves in warm dilute alkalis, and the solution, on acidifying and extracting with ether, yields *cis*- $\alpha\gamma$ -trimethylglutaconic acid,  $\begin{array}{c} \text{CO}_2\text{H}\cdot\text{CMe}_2\cdot\text{CH} \\ \text{CO}_2\text{H}\cdot\text{CMe}_2\cdot\text{H} \end{array}$ , as a colourless, crystalline substance which melts at  $125^\circ$ .

When this acid is treated with bromine, it is readily converted into *cis*- $\beta\gamma$ -dibromo- $\alpha\gamma$ -trimethylglutaric acid,

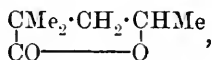


which melts at  $168^\circ$  and is isomeric with the corresponding *trans*-acid described in the previous paper (*loc. cit.*, p. 779). It was stated above that the *trans*-hydroxy-acid, when heated in small quantities, distils with little decomposition, and we now find that, when considerable quantities of the acid are slowly heated, decomposition sets in, and a semi-solid distillate is obtained which consists of the above-mentioned anhydride of *cis*-trimethylglutaconic acid and an oily acid boiling at about  $213^\circ$ .

The latter is *crotonyldimethylacetic acid*, produced from  $\alpha\gamma$ -trimethylglutaconic acid by the elimination of carbon dioxide according to the equation:



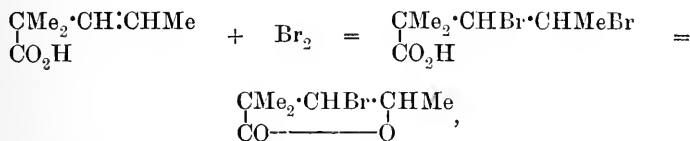
Crotonyldimethylacetic acid is also formed in considerable quantities during the preparation of the anhydride of *cis*-trimethylglutaconic acid by the distillation of *cis*-hydroxytrimethylglutaric acid (see above). It is an unsaturated acid which, when digested with dilute sulphuric acid, is converted into the lactone of  $\gamma$ -hydroxy- $\alpha\gamma$ -trimethylbutyric acid,



a substance which has already been described by Anschütz and Gillet (*Annalen*, 1888, 247, 107), who obtained it from *aa*-dimethylævulic acid,  $\text{CO}_2\text{H}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{COMe}$ , by reduction with sodium amalgam and named it  $\alpha$ -dimethylvalerolactone.

When crotonyldimethylacetic acid is treated with bromine, the colour rapidly disappears, but, even at low temperatures and in the dark, hydrogen bromide is eliminated. The product of this reaction—

a neutral, crystalline substance melting at  $83^\circ$ —is evidently the *lactone* of  $\beta$ -bromo- $\gamma$ -hydroxy- $\alpha\alpha\gamma$ -trimethylbutyric acid, produced in the following way :



but the ease with which the dibromo-acid loses hydrogen bromide is very unusual.

*cis- $\alpha\alpha\gamma$ -Trimethylglutaconic Acid*,  $\text{CO}_2\text{H} \cdot \text{CMe}_2 \cdot \text{CH} : \text{CMe} \cdot \text{CO}_2\text{H}$ .

In preparing this acid, pure *cis*-hydroxytrimethylglutaric acid was rapidly distilled in small quantities and under the ordinary pressure, when carbon dioxide and water vapour were given off and an oily distillate was obtained, which, on cooling, became semi-solid; this mass was cooled in a freezing mixture and collected at the pump on a funnel surrounded with ice and salt, the residue being then left in contact with porous porcelain until the oily impurity had been completely absorbed. By recrystallisation from light petroleum, colourless needles were obtained which melted at  $88^\circ$ .

0.1239 gave 0.2829  $\text{CO}_2$  and 0.0748  $\text{H}_2\text{O}$ .  $\text{C} = 62.7$ ;  $\text{H} = 6.7$ .

$\text{C}_8\text{H}_{10}\text{O}_3$  requires  $\text{C} = 62.3$ ;  $\text{H} = 6.5$  per cent.

The *anhydride* of *cis-trimethylglutaconic acid* is very readily soluble in chloroform and in ether, less so in cold benzene, and sparingly so in cold light petroleum. The solution in chloroform does not decolorise bromine, and when the benzene solution is mixed with aniline, no crystalline anilic acid separates. The anhydride is almost insoluble in cold water, but it dissolves on warming and is not at once hydrolysed, since, if the solution is rapidly cooled and shaken, a considerable amount of the anhydride crystallises out unchanged. It is insoluble in cold sodium carbonate solution, but dissolves readily in warm dilute aqueous caustic potash, and on acidifying a clear solution is obtained. In order to isolate the very readily soluble *cis*-acid, the liquid was saturated with ammonium sulphate, when the acid separated in needles; the whole was then extracted three times with ether, the ethereal solution dried over calcium chloride and evaporated, and the solid residue purified by recrystallisation from a very small quantity of water.

0.1507 gave 0.3103  $\text{CO}_2$  and 0.0945  $\text{H}_2\text{O}$ .  $\text{C} = 56.2$ ;  $\text{H} = 7.0$ .

$\text{C}_8\text{H}_{12}\text{O}_4$  requires  $\text{C} = 55.8$ ;  $\text{H} = 7.0$  per cent.

*cis*- $\alpha\alpha\gamma$ -Trimethylglutaconic acid melts at about  $125^\circ$  with evolution of gas and is readily soluble in water, chloroform, benzene, alcohol, or ether; its solution in aqueous sodium carbonate decolorises permanganate, but not instantaneously. When the acid is exposed to dry bromine vapour for about three hours and the excess of bromine removed over caustic potash in a vacuum desiccator, a solid residue is obtained which crystallises from formic acid (sp. gr. 1.22), in which it is very sparingly soluble, in hard, crystalline crusts. The analysis shows that this acid, which melts at about  $168^\circ$  with decomposition, is *cis*- $\beta\gamma$ -dibromo- $\alpha\alpha\gamma$ -trimethylglutaric acid,  $\text{CO}_2\text{H}\cdot\text{CMe}_2\cdot\text{CHBr}\cdot\text{CMeBr}\cdot\text{CO}_2\text{H}$ .

0.1929 gave 0.2180 AgBr. Br = 48.1.

$\text{C}_8\text{H}_{12}\text{O}_4\text{Br}_2$  requires Br = 48.2 per cent.

*Crotonyldimethylacetic Acid*,  $\text{CO}_2\text{H}\cdot\text{CMe}_2\cdot\text{CH}\cdot\text{CHMe}$ .

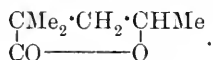
The oily filtrate, which had been separated from the crystals of the anhydride of *cis*-trimethylglutaconic acid, was dissolved in ether and the ethereal solution extracted with sodium carbonate, by which means the crotonyldimethylacetic acid is dissolved, whereas the above anhydride, which is still present in considerable quantities, remains in the ether.

After acidifying and extracting with ether, an oily acid was obtained which distilled at  $210$ — $220^\circ$ , and as this still contained traces of anhydride, the treatment with sodium carbonate was repeated and the acid again distilled, when almost the whole quantity passed over at  $213^\circ$  as a colourless oil having a penetrating and most disagreeable odour.

0.1291 gave 0.3088  $\text{CO}_2$  and 0.1101  $\text{H}_2\text{O}$ . C = 65.2; H = 9.4.

$\text{C}_7\text{H}_{12}\text{O}_2$  requires C = 65.6; H = 9.4 per cent.

When boiled with 25 per cent. sulphuric acid for a few minutes, crotonyldimethylacetic acid is readily and almost completely converted into the lactone of  $\gamma$ -hydroxy- $\alpha\alpha\gamma$ -trimethylbutyric acid,



The product was extracted with ether, the ethereal solution washed with dilute aqueous sodium carbonate, dried over calcium chloride, and evaporated, when a colourless oil remained, which smelt strongly of camphor and crystallised on cooling. The crystals, when left in contact with porous porcelain until quite dry, melted at  $48$ — $52^\circ$ .

0.1760 gave 0.4232  $\text{CO}_2$  and 0.1494  $\text{H}_2\text{O}$ . C = 65.5; H = 9.4.

$\text{C}_7\text{H}_{12}\text{O}_2$  requires C = 65.5; H = 9.4 per cent.

This lactone has already been prepared by Anschütz and Gillet

(*Annalen*, 1888, 247, 107,) who give  $52^\circ$  as the melting point. Crotonyldimethylacetic acid dissolves in chloroform, and if the solution is treated with bromine at the ordinary temperature the colour disappears, heat is generated, and a considerable quantity of hydrogen bromide is produced. This formation of hydrogen bromide cannot be avoided by keeping the chloroform solution in a blackened test tube at  $0^\circ$  and adding the bromine slowly. On allowing the product of bromination to evaporate spontaneously, a colourless residue is obtained, which crystallises from light petroleum (b. p.  $50-60^\circ$ ) in long prisms and melts at  $82-83^\circ$ .

0.3020 gave 0.2748 AgBr. Br = 38.8.

$C_7H_{11}O_2Br$  requires Br = 38.7 per cent.

As stated in the introduction, this substance is evidently the *lactone* of  $\beta$ -bromo- $\gamma$ -hydroxy- $\alpha\gamma$ -trimethylbutyric acid.

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### XVIII.—*Derivatives of $\beta$ -Resorcylic Acid and of Protocatechuic Acid.*

By WILLIAM HENRY PERKIN, jun., and EMANUEL SCHIESS.

DURING the course of a long series of researches on the constitution of brazilin and hæmatoxylin, it was found necessary, for the purposes of comparison, to prepare and investigate several new derivatives of resorcinol and catechol, and in this paper we give a brief account of some of the compounds which were thus prepared.

*Dimethylresorcylic Acid*,  $(MeO)_2C_6H_3 \cdot CO_2H$ , and its *Methyl and Ethyl Esters*.

*Methyl dimethyl- $\beta$ -resorcylicate*,  $(MeO)_2C_6H_3 \cdot CO_2Me$ , is readily obtained when  $\beta$ -resorcylic acid is treated with caustic potash and methyl sulphate in aqueous solution. It is thus seen that the hydroxyl group in  $\beta$ -resorcylic acid, which is in the *o*-position with respect to the carbonyl group, may be methylated by means of aqueous caustic potash and methyl sulphate, whereas, as is well known, the hydroxyl group in the above position in this and other similar compounds is hardly attacked by the usual treatment with alcoholic potash and methyl iodide.

$\beta$ -Resorecylic acid (30 grams) is dissolved in 240 grams of 10 per

cent. aqueous caustic soda, and then methyl sulphate (65 grams) added in small quantities at a time. After each addition, the bottle containing the mixture is vigorously shaken on the machine and cooled, if necessary, no further quantity being added until the last portion has been completely decomposed. Care is also taken, by adding small quantities of strong caustic soda solution from time to time, that the liquid is always strongly alkaline. The oil which separates is extracted with ether, the ethereal solution washed with dilute aqueous caustic soda, dried over calcium chloride, and evaporated, and the residual oil fractionated under reduced pressure, when almost the whole distils at 160—162° (13 mm.). The boiling point of this oil under the ordinary pressure was observed to be 294—296°.

0.2261 gave 0.4978 CO<sub>2</sub> and 0.1126 H<sub>2</sub>O. C = 60.9 ; H = 6.1.

C<sub>10</sub>H<sub>12</sub>O<sub>4</sub> requires C = 61.2 ; H = 6.1 per cent.

The yield of methyl dimethyl-β-resorcyate (which does not appear to have been previously prepared) varies considerably, but is usually 30—40 per cent. of the theoretical. As, however, by acidifying the alkaline liquids, quantities of methyl- and dimethyl-β-resorcylic acids may be precipitated and used in a subsequent operation, the total yield from a given quantity of β-resorcylic acid is actually much greater than this. When the above methyl ester is boiled with alcoholic potash for a few minutes and the solution, after evaporating with water, acidified with hydrochloric acid, dimethyl-β-resorcylic acid separates at once, and after recrystallising melts at 108°.

*Ethyl Dimethyl-β-resorcyate*, (MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·CO<sub>2</sub>Et.

This ester was prepared by boiling dimethyl-β-resorcylic acid with alcohol and sulphuric acid for about 6 hours, and then adding water and extracting with ether. After washing with sodium carbonate, drying over calcium chloride, and distilling off the ether, an oil was obtained which distilled constantly at 170° under 13 mm. pressure.

0.1337 gave 0.3080 CO<sub>2</sub> and 0.0826 H<sub>2</sub>O. C = 62.8 ; H = 6.9.

C<sub>11</sub>H<sub>14</sub>O<sub>4</sub> requires C = 62.9 ; H = 6.7 per cent.

*2:4-Dimethoxybenzoylacetophenone*, (MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·CO·CH<sub>2</sub>·CO·C<sub>6</sub>H<sub>5</sub>.

This substance is produced by the condensation of ethyl β-resorcyate and acetophenone in the presence of sodium, and in our first experiments, which were carried out under ordinary conditions (see, for example, Kostanecki, Różycki, and Tambor, *Ber.*, 1900, **33**, 3413), great difficulty was experienced in isolating more than traces of the crystalline product of the reaction. On using, however, conditions

similar to those recommended by the Farbwerke vorm. Meister, Lucius, and Brüning (*Ber.*, 1890, 23, *Ref.* 40; see also Bülow and Riess, *ibid.*, 1902, 35, 3902), we were able to obtain an excellent yield of 2:4-dimethoxybenzoylacetophenone. Ethyl dimethyl- $\beta$ -resorcyate (21 grams) is dissolved in dry ether, mixed with acetophenone (12 grams) and treated with finely divided sodium (2.5 grams).<sup>\*</sup> Any rise of temperature is prevented by placing the flask in ice-water, the reaction is promoted by repeated shaking, and after two hours the flask is allowed to remain overnight at the ordinary temperature. The sodium gradually passes into solution and the sodium compound separates as a crystalline powder, the whole ultimately becoming a semi-solid mass. In order to isolate the dimethoxybenzoylacetophenone, the product is made slightly acid by the addition of dilute acetic acid, extracted with ether, the ethereal solution washed with dilute sodium carbonate solution and well agitated on the machine with aqueous copper acetate until no further separation of the green copper derivative takes place. This is collected at the pump, washed with water and alcohol, and purified by recrystallisation from benzene, from which the copper derivative of 2:4-dimethoxybenzoylacetophenone separates in slender, green needles containing one molecule of benzene of crystallisation.<sup>†</sup>

0.2335 gave 0.0259 CuO. Cu = 8.6.

$C_{34}H_{30}O_8Cu, C_6H_6$  requires Cu = 8.4 per cent.

After drying at 110° until constant, the following complete analysis was made:

0.1803 gave 0.4277 CO<sub>2</sub>, 0.0778 H<sub>2</sub>O, and 0.0226 CuO.

C = 64.7; H = 4.8; Cu = 10.0.

$C_{34}H_{30}O_8Cu$  requires C = 64.9; H = 4.8; Cu = 10.0 per cent.

The pure copper compound was then mixed with excess of dilute hydrochloric acid and the diketone extracted with ether, the ethereal solution was washed with water until free from copper, dried over calcium chloride, and evaporated, when an oil was obtained which rapidly solidified. The substance was further purified by recrystallisation from alcohol, from which it separates in plates.

0.1501 gave 0.3948 CO<sub>2</sub> and 0.0779 H<sub>2</sub>O. C = 71.7; H = 5.8.

$C_{17}H_{16}O_4$  requires C = 71.8; H = 5.7 per cent.

2:4-Dimethoxybenzoylacetophenone melts at 55° and is readily soluble

<sup>\*</sup> This condition is best obtained by melting the sodium under boiling toluene and then shaking vigorously.

<sup>†</sup> It is noteworthy that the copper derivative of 3:5-dimethoxybenzoylacetophenone also crystallises with one molecule of benzene (Bülow and Riess, *loc. cit.*).

in benzene, ether, and chloroform, more sparingly in alcohol and light petroleum. Its solution in alcohol gives with ferric chloride an intense reddish-brown coloration.

2 : 4-Dimethoxycinnamic Acid,  $(\text{MeO})_2\text{C}_6\text{H}_3\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{H}$ .

This acid was first obtained from umbelliferone by Will and Tiemann (*Ber.*, 1882, 15, 2080 ; 1883, 16, 2116) in two forms— $\alpha$ - and  $\beta$ -—which melt at  $138^\circ$  and  $184^\circ$  respectively, and obviously represent the *cis*- and *trans*-modifications of the acid. Since it was probable that we should require considerable quantities of this acid, a number of experiments were made with the object of preparing the substance synthetically, with the result that two methods were devised by which it may be readily obtained in quantity from dimethyl- $\beta$ -resorcyraldehyde.

*Method I. Preparation of 2 : 4-Dimethoxycinnamic Acid from Dimethyl- $\beta$ -resorcyraldehyde by the Action of Sodium Acetate and Acetic Anhydride.*

Dimethyl- $\beta$ -resorcyraldehyde (10 grams) is intimately mixed with anhydrous sodium acetate (10 grams) and heated with acetic anhydride (30 grams) in a reflux apparatus for 20 hours in an oil-bath at  $170^\circ$ . The brown mass is diluted with water and the excess of acetic acid removed by distillation in steam, the residue is then made alkaline by adding sodium carbonate, and allowed to remain until quite cold. The unchanged aldehyde which separates is filtered off, the filtrate acidified with hydrochloric acid, and the very sparingly soluble dimethoxycinnamic acid, which separates at once, collected and purified by recrystallisation from acetic acid. The acid thus obtained is the  $\beta$ -modification and melts at  $186^\circ$ .

0.1420 gave 0.3317  $\text{CO}_2$  and 0.0780  $\text{H}_2\text{O}$ .  $\text{C} = 63.7$  ;  $\text{H} = 6.1$ .

$\text{C}_{11}\text{H}_{12}\text{O}_4$  requires  $\text{C} = 63.5$  ;  $\text{H} = 5.8$  per cent.

*Method II. Preparation of Ethyl 2 : 4-Dimethoxycinnamate,  $(\text{MeO})_2\text{C}_6\text{H}_3\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{Et}$ , by the Condensation of Dimethyl- $\beta$ -resorcyraldehyde with Ethyl Acetate in the presence of Sodium.*

This ethyl ester was first prepared by the esterification of the acid with alcohol and sulphuric acid, and was thus obtained as a crystalline solid which melted at  $61^\circ$  and distilled at  $210\text{--}212^\circ$  under 13 mm. pressure. Subsequently it was discovered that it can be obtained directly, and in a yield of at least 80 per cent. of the theoretical amount, by

the general method devised by Claisen (*Ber.*, 1890, 23, 977), and which appears to be not nearly so well known as it deserves to be. Dimethyl- $\beta$ -resorcyraldehyde (16.6 grams) is dissolved in 30 grams of ethyl acetate (which has been carefully freed from water and alcohol) and then finely divided sodium (2.5 grams, see foot-note, p. 161) added all at once. The sodium begins to act immediately, and, after two hours in ice-water, the mixture is left overnight at the ordinary temperature, when all the sodium will have disappeared. The dark brown liquid is acidified with dilute acetic acid, extracted with ether, the ethereal solution well washed, dried over calcium chloride, and evaporated, when an oil is obtained which rapidly solidifies. In purifying this substance, it is best to distil the product first under reduced pressure, when almost the whole passes over at  $208\text{--}212^\circ$  (13 mm.), leaving only a small quantity of resinous matter in the retort. The distillate, which solidifies at once, is pure enough for most experiments, but for analysis the substance was recrystallised from light petroleum, from which it separated in slender needles melting at  $61^\circ$ .

0.1518 gave 0.3668  $\text{CO}_2$  and 0.0941  $\text{H}_2\text{O}$ . C = 65.9; H = 6.9.

$\text{C}_{13}\text{H}_{16}\text{O}_4$  requires C = 66.1; H = 6.8 per cent.

*Ethyl 2:4-dimethoxycinnamate* is readily soluble in alcohol, ether, or benzene, but sparingly so in cold light petroleum. Attempts were made to convert this ester into ethyl dimethoxyphenyl- $\alpha\beta$ -dibromopropionate by the action of bromine, but, so far, these have not been successful. When bromine is added to the chloroform solution of the ester, dark decomposition products are formed, and hydrogen bromide is evolved even at  $0^\circ$ . Possibly under different conditions, a method of avoiding this decomposition and substitution may be found, and further experiments with this end in view are in progress.

### 3:4-Dimethoxycinnamic Acid, $(\text{MeO})_2\text{C}_6\text{H}_3\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{H}$ .

The methyl ester of this acid is formed when 3:4-dihydroxycinnamic acid (caffeic acid) or either of its two isomeric 3- and 4-monomethyl derivatives,  $(\text{MeO})(\text{OH})\text{C}_6\text{H}_3\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{H}$ , called respectively ferulic and isoferulic acids, is heated with methyl iodide and caustic potash in methyl alcoholic solution (Tiemann and Nagai, *Ber.*, 1878, 11, 652; Tiemann and Will, *ibid.*, 1881, 14, 959).

The melting point of the methyl ester is given as  $64^\circ$ , and that of the free acid as  $180\text{--}181^\circ$ . Although 2:4-dimethoxycinnamic acid (see p. 162) exists in two well-defined stereoisomeric forms, the 3:4-dimethoxy-acid has, so far, only been obtained in the one modification. In our experiments on the synthesis of 3:4-dimethoxycinnamic acid, we employed in the first instance an exactly similar

process to that described in the case of the 2:4-dimethoxy-acid, that is, we heated a mixture of 3:4-dimethoxybenzaldehyde (dimethylcatecholaldehyde) and sodium acetate with acetic anhydride. The yield of acid obtained was upwards of 50 per cent. of the aldehyde employed, and a good deal of the latter was recovered unchanged. 3:4-Dimethoxycinnamic acid melts at  $180^\circ$  and crystallises from acetic acid in needles; it is very sparingly soluble in water.

0.1439 gave 0.3358  $\text{CO}_2$  and 0.0739  $\text{H}_2\text{O}$ .  $\text{C} = 63.6$ ;  $\text{H} = 5.7$ .

$\text{C}_{11}\text{H}_{12}\text{O}_4$  requires  $\text{C} = 63.5$ ;  $\text{H} = 5.8$  per cent.

*Ethyl 3:4-Dimethoxycinnamate*,  $(\text{MeO})_2\text{C}_6\text{H}_3\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{Et}$ .

When 3:4-dimethoxybenzaldehyde is condensed with ethyl acetate under the conditions described in the case of the preparation of the ethyl salt of the 2:4-dimethoxy-acid (p. 162) and the product purified by fractionation, ethyl 3:4-dimethoxycinnamate is readily obtained pure and in a yield of 85 per cent. of that theoretically possible. It crystallises from light petroleum in plates, melts at  $59^\circ$ , and distils at  $196\text{--}197^\circ$  under 13 mm. pressure.

0.1507 gave 0.3642  $\text{CO}_2$  and 0.0936  $\text{H}_2\text{O}$ .  $\text{C} = 65.9$ ;  $\text{H} = 6.9$ .

$\text{C}_{13}\text{H}_{16}\text{O}_4$  requires  $\text{C} = 66.1$ ;  $\text{H} = 6.8$  per cent.

It dissolves readily in alcohol, benzene, or chloroform, but is sparingly soluble in light petroleum.

*Ethyl 3:4-Dimethoxyphenyl- $\alpha\beta$ -dibromopropionate*,

$(\text{MeO})_2\text{C}_6\text{H}_3\cdot\text{CHBr}\cdot\text{CHBr}\cdot\text{CO}_2\text{Et}$ ,

and *3:4-Dimethoxyphenylpropionic Acid*,

$(\text{MeO})_2\text{C}_6\text{H}_3\cdot\text{C}:\text{C}\cdot\text{CO}_2\text{H}$ .

In its behaviour towards bromine, ethyl 3:4-dimethoxycinnamate shows much greater stability than the corresponding 2:4-dimethoxy-compound (p. 163), and this enabled us to prepare, without much difficulty, considerable quantities of the dibromo-additive product in a pure condition. Ethyl 3:4-dimethoxycinnamate (23.6 grams) is dissolved in chloroform (40 grams), the solution cooled with ice-water, and then 16 grams of bromine, dissolved in 30 grams of chloroform, gradually added. When the colour of the bromine has disappeared, the chloroform is removed at as low a temperature as possible, by distillation under reduced pressure, and the oily residue then solidifies to a hard, yellow, crystalline cake. After triturating with cold light petroleum and filtering at the pump, the substance is then crystallised from the same solvent.

0.2218 gave 0.2092 AgBr. Br = 40.2.

$C_{13}H_{16}O_4Br_2$  requires Br = 40.4 per cent.

*Ethyl 3:4-dimethoxyphenyl- $\alpha\beta$ -dibromopropionate* crystallises from light petroleum in colourless needles and melts at 110—111°; it is readily soluble in alcohol, ether, benzene, chloroform, or hot light petroleum, but sparingly so in the latter solvent in the cold.

*3:4-Dimethoxyphenylpropionic acid* is readily obtained when ethyl 3:4-dimethoxyphenyl- $\alpha\beta$ -dibromopropionate (1 mol.) is digested for 8 hours with a large excess of alcoholic potash (6 mols.). The product is evaporated on the water-bath to remove the bulk of the alcohol, the residue dissolved in water, and neutralised with hydrochloric acid. After filtering from a small quantity of dark resinous matter which usually separates, the clear solution is acidified, when the new acid is precipitated in white flocks. It is collected at the pump, washed thoroughly with water, dried on porous porcelain, and purified by recrystallisation from benzene.

0.1426 gave 0.3338  $CO_2$  and 0.0694  $H_2O$ . C = 63.9; H = 5.0.

$C_{11}H_{10}O_4$  requires C = 64.1; H = 4.8 per cent.

*3:4-Dimethoxyphenylpropionic acid* melts at 149° with decomposition and is readily soluble in alcohol, but sparingly so in cold benzene or chloroform; it dissolves very sparingly in hot water and is almost insoluble in the cold; it crystallises best from benzene, from which it separates in colourless, microscopic needles.

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## XIX.—*The Formation of Phloroglucinol by the Interaction of Ethyl Malonate with its Sodium Derivative.*

By CHARLES WATSON MOORE.

IN the year 1885, Baeyer made the important discovery that when ethyl malonate is heated with its sodium derivative at 145°, condensation takes place and a derivative of phloroglucinol is formed which melts at 104°, and which Baeyer considered was ethyl phloroglucinoltricarboxylate,  $C_6(OH)_3(CO_2Et)_3$  (*Ber.*, 1885, 18, 3457).

During the course of an investigation involving the use of ethyl malonate, the author was led to reinvestigate this matter, and has been able to prove that the substance formed under the conditions employed

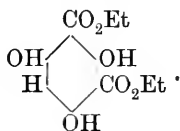
by Baeyer is ethyl phloroglucinoldicarboxylate,  $C_6H(OH)_3(CO_2Et)_2$ , and not the above-mentioned tricarboxylate.

Since the difference in percentage composition between these two esters is small (a fact which accounts for the mistakes which have arisen as to its composition), the molecular weight was determined in benzene solution by the cryoscopic method, and two determinations gave 270 and 273, whereas the molecular weights of the dicarboxylic and tricarboxylic esters are 270 and 342 respectively.

The determination of the ethoxyl groups, which was kindly carried out by Dr. W. H. Perkin, sen., in his new modification of Zeisel's apparatus (Trans., 1903, 83, 1367), also gave numbers which clearly show that the substance is a dicarboxylic ester.

When treated with bromine, it yields a bromo-compound having the composition  $C_6Br(OH)_3(CO_2Et)_2$ , which was first prepared by Oscar Bally (*Ber.*, 1888, 21, 1770), the process being a simple case of substitution of hydrogen by bromine, whereas Bally, who supposed that the original ester was the tricarboxylic ester, was forced to assume that, during bromination, elimination of ethyl bromide and carbon dioxide had taken place, in order to account for the composition of the bromo-compound. If then the product of the condensation of ethyl malonate with its sodium compound is the dicarboxylic ester, it follows that during the condensation, elimination of ethyl alcohol and carbon dioxide must have taken place, and, in proof of this, the author finds that the mixture invariably contains considerable quantities of sodium carbonate.

Since ethyl phloroglucinoldicarboxylate readily yields a triacetyl compound when heated with acetic anhydride, there can scarcely be a doubt that its constitution is represented by the formula :



*Ethyl Phloroglucinoldicarboxylate*,  $C_6H(OH)_3(CO_2Et)_2$ .

During this investigation, the above ester was repeatedly prepared according to the directions given by Baeyer (*loc. cit.*), but the purification was found to be tedious, for the compound, as Baeyer states, is yellow, and the alcoholic solution must be boiled for a long time with animal charcoal before the yellow colour can be removed. The pure ester, after repeated crystallisation, melted at  $107^\circ$  (Baeyer gives  $104^\circ$ ), and was analysed with the following result :

0.2014 gave 0.3944 CO<sub>2</sub> and 0.0948 H<sub>2</sub>O. C = 53.4; H = 5.2.

C<sub>6</sub>H(OH)<sub>3</sub>(CO<sub>2</sub>Et)<sub>2</sub> requires C = 53.3; H = 5.2 per cent.

C<sub>6</sub>(OH)<sub>3</sub>(CO<sub>2</sub>Et)<sub>3</sub> „ C = 52.6; H = 5.2 „

The analytical numbers given by Baeyer are C = 52.4; H = 5.2 per cent. As the difference in the percentage composition of the di- and tri-carboxylic esters is so small, the molecular weight was determined by the cryoscopic method, using benzene as the solvent. Two experiments gave the values 270 and 273, whereas the molecular weight of the dibasic ester, C<sub>12</sub>H<sub>14</sub>O<sub>7</sub>, is 270, and that of the tribasic ester, C<sub>15</sub>H<sub>18</sub>O<sub>9</sub>, is 342.

The view that the ester is ethyl phloroglucinoldicarboxylate received further confirmation from the determination of the ethoxyl groups by Dr. W. H. Perkin.\*

0.3436 gave 0.5641 AgI, corresponding with OEt = 31.5.

0.3504 „ 0.5807 AgI, „ „ „ = 31.8.

The dibasic ester, C<sub>12</sub>H<sub>14</sub>O<sub>7</sub>, contains OEt = 33.3 per cent.

The tribasic ester, C<sub>15</sub>H<sub>18</sub>O<sub>9</sub>, „ OEt = 39.4 „

*Ethyl Triacetylphloroglucinoldicarboxylate*, C<sub>6</sub>H(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>3</sub>(CO<sub>2</sub>Et)<sub>2</sub>.

This substance, which has already been described by Oscar Bally (*Ber.*, 1888, 21, 1768), was prepared by his method. After repeated recrystallisation from alcohol, it was obtained as a colourless, crystalline mass which melted at 96° (the m. p. 75—76° given by Bally is evidently a clerical error).

0.1488 gave 0.2970 CO<sub>2</sub> and 0.0690 H<sub>2</sub>O. C = 54.4; H = 5.1.

C<sub>18</sub>H<sub>20</sub>O<sub>10</sub> requires C = 54.5; H = 5.0 per cent.

Bally found C = 53.9 and H = 5.0, a result which agrees fairly well with the above, but he assumed that his substance was the triacetyl compound of ethyl phloroglucinoltricarboxylate.

*Ethyl Bromophloroglucinoldicarboxylate*, C<sub>6</sub>Br(OH)<sub>3</sub>(CO<sub>2</sub>Et)<sub>2</sub>.

This substance was first obtained by Bally (*loc. cit.*) by treating the ester prepared by Baeyer's process with bromine in chloroform solution. In this preparation also, Bally's directions were carefully followed and the bromo-compound was obtained, exactly as he describes, in colourless needles melting at 128°. The results obtained on analysis were: C = 40.9; H = 3.7; Br = 22.8.

C<sub>12</sub>H<sub>13</sub>O<sub>7</sub>Br requires C = 41.2; H = 3.7; Br = 22.8 per cent.

\* The determination of ethoxyl groups always gives figures rather lower than the theoretical, the loss being apparently due to the conversion of a small amount of the ethyl iodide into ethylene during the process

The analytical results obtained by Bally agree fairly well with those just given, and it is curious that he should assume, in order to explain the composition of this bromo-compound, that, during the bromination, carbon dioxide and ethyl bromide are eliminated, thus converting ethyl phloroglucinoltricarboxylate into ethyl bromophloroglucinoldicarboxylate, whereas there is no indication of any such elimination of carbon dioxide.

That carbon dioxide is formed during the condensation of ethyl malonate with its sodium compound by the process recommended by Baeyer was proved by carrying out the operation in a flask fitted with a dropping funnel, and through which hydrogen was passing during the whole operation. On adding hydrochloric acid through the dropping funnel to the product and leading the gases through baryta water, it was at once seen that quantities of carbon dioxide were being evolved.

*Preparation of Ethyl Phloroglucinoldicarboxylate by Heating Ethyl Sodiomalonate with Ethyl Malonate in Alcoholic Solution.*

This method, which gives a pure product much more readily than that described by Baeyer, was carried out as follows.

Sodium (14.4 grams) is dissolved in alcohol (200 grams) and, when nearly cold, mixed with 200 grams of ethyl malonate. The mixture, while still warm, is transferred to soda-water bottles and heated in a boiling brine bath at 105—108° for 15 hours. The white precipitate, which separates during this operation, consists of the sodium compound of ethyl phloroglucinoldicarboxylate mixed with sodium carbonate; it is collected at the pump, washed with alcohol, and then dissolved in water acidified with hydrochloric acid, when carbon dioxide is evolved and the ester precipitated as an almost colourless crystalline mass. After one crystallisation from alcohol, the ester was perfectly colourless and melted at 106—107°.

0.1736 gave 0.3393  $\text{CO}_2$  and 0.0815  $\text{H}_2\text{O}$ .  $\text{C} = 53.3$ ;  $\text{H} = 5.2$ .

$\text{C}_6\text{H}(\text{OH})_3(\text{CO}_2\text{Et})_2$  requires  $\text{C} = 53.3$ ;  $\text{H} = 5.2$  per cent.

This ester yields phloroglucinol on hydrolysis, and its identity with the ester prepared by Baeyer's process was proved by mixing equal quantities of the two specimens when there was no alteration in the melting point.

The yield obtained in alcoholic solution is practically the same as that obtained by Baeyer's process, but a large amount of ethyl malonate may be recovered and used in a subsequent operation.

XX.—*The Resolution of dl-Methylhydrindamine. Isomeric Salts of d- and l-Methylhydrindamines with d-Chlorocamphorsulphonic Acid.*

By GEORGE TATTERSALL, B.Sc.

IN a recent communication (Tattersall and Kipping, Trans., 1903, 83, 918), a method was described by which *dl*-methylhydrindamine could be resolved into its enantiomorphously related components by the use of *d*-bromocamphorsulphonic acid. As the yield of these salts of the *d*- and *l*-bases was always small compared with the quantity of original material taken, and also varied considerably with the conditions of the experiment, the author, at Dr. Kipping's suggestion, attempted to find a more satisfactory process for the resolution of the *dl*-base.

Experiments then showed that *d*-tartaric acid is a more suitable agent with which to effect the resolution. When a solution of this acid is added to *dl*-methylhydrindamine in sufficient quantity to form the hydrogen tartrate and the product fractionated from water at the ordinary temperature, an excellent separation of the *d*- and *l*-bases is effected. The most sparingly soluble fractions, which contain the hydrogen tartrate of the *d*-base in a pure condition, amount to about one-third of the whole material.

The purification of the bases was carried out by converting the first fractions, containing chiefly the *d*-base, and the last fractions (the remaining two-thirds) into the *d*-bromocamphorsulphonates separately, and finally fractionating the products by crystallising from water.

The production of isomeric salts by the combination of *d*- and *l*-methylhydrindamines with *d*-bromocamphorsulphonic acid has been already described (Tattersall and Kipping, *loc. cit.*), and in this paper an account is given of similar experiments made with *d*-chlorocamphorsulphonic acid and the same bases.

The salt of each base, prepared from very carefully purified materials, was subjected to repeated fractional crystallisation and the final fractions examined. In both cases, the melting points of successive fractions were found to decrease from the first to the last, this behaviour corresponding with that observed in the case of the bromocamphorsulphonates. An important point of difference between the chlorocamphorsulphonates and the bromocamphorsulphonates, however, is that in the case of the former acid the specific rotations of the last fractions are higher than those of the first fractions, whereas with the latter acid the reverse is the case. These generalisations are true

both for aqueous and chloroform solutions. The following table summarises the results obtained :

*l*-Methylhydrindamine *d*-chlorocamphorsulphonate.

	M. p.	[ $\alpha$ ] <sub>D</sub> .	
		In chloroform.	In water.
First fraction	239°	+ 3.3°	+ 34.2°
Last     ,,	231—233°	8.0	35.8

*d*-Methylhydrindamine *d*-chlorocamphorsulphonate.

	M. p.	[ $\alpha$ ] <sub>D</sub> .	
		In chloroform.	In water.
First fraction	247°	+ 56°	+ 60°
Last     ,,	225—230°	63	63

These results are similar to those obtained with the hydrindamine *d*-chlorocamphorsulphonates (Kipping, Trans., 1903, 83, 902), but it was not found possible to isolate the isomerides of higher specific rotation.

#### EXPERIMENTAL.

About 30 grams of purified *dl*-methylhydrindamine *d*-bromocamphorsulphonate, obtained as previously described (Tattersall and Kipping, *loc. cit.*), was decomposed with barium hydroxide and the base distilled in steam. A solution of *d*-tartaric acid was added to the distillate until the latter was just acid, and then a further equal quantity of acid in order that the hydrogen tartrate might be produced. The solution was evaporated and the salt fractionally crystallised. The first deposit on recrystallisation was obtained in vitreous prisms, whilst the mother liquors slowly deposited clusters of small, opaque crystals. When the fractionation had proceeded so far that the first deposit had been twice crystallised, the first two fractions were examined. The first was found to be hydrated and when dried, melted at about 150°; the second was almost anhydrous and melted at 190° (approximately). The fractions were therefore different.

The first fraction, amounting to about one-fourth or one-third of the whole, was decomposed with caustic potash, the base distilled in steam, the distillate neutralised with *d*-bromocamphorsulphonic acid, and the solution evaporated and crystallised, when the salt of *d*-methylhydrindamine was obtained. The sparingly soluble fractions of the hydrogen tartrate therefore contain the *d*-base.

Owing to the difficulty usually experienced in obtaining a pure salt

from the mother liquors, and considering the great ease with which *dl*-methylhydrindamine *d*-bromocamphorsulphonate can be separated from the salt of the *d*- or *l*-base, the last fractions were decomposed with caustic potash, the base distilled in steam and combined with *d*-bromocamphorsulphonic acid. On crystallising, the salt of *l*-methylhydrindamine first separated and the salt of the *dl*-base was found in the mother liquors.

The *d*-base can, obviously, be obtained pure from the first deposits of the hydrogen tartrate, but the purification of the *l*-base was always carried out by converting the last fractions into the *d*-bromocamphorsulphonate.

By this process, about two-thirds of the original *dl*-base can be resolved into its enantiomorphously related components.

*d*-Methylhydrindamine Hydrogen Tartrate,  $C_{10}H_{13}N, C_4H_6O_6, 2H_2O$ .—This salt crystallises from water in long, vitreous, hydrated prisms which become opaque on warming in contact with a solution of the salt; it is moderately soluble in alcohol or water, but more sparingly so in the latter solvent than the corresponding salt of the *l*-base, and is practically insoluble in chloroform, ether, ethyl acetate, and light petroleum. The melting point of the dried salt is  $153-155^\circ$ , being somewhat indefinite owing to slight decomposition.

The water was estimated in air-dried samples by determining the loss of weight at  $100^\circ$ .

2.6761 lost 0.2868.  $H_2O = 10.7$ .

$C_{10}H_{13}N, C_4H_6O_6, 2H_2O$  requires  $H_2O = 10.8$  per cent.

The specific and molecular rotations were determined in aqueous solution with samples of the anhydrous salt, 20 c.c. of solution being used.\*

Weight of salt.	$\alpha_D$ .	$[\alpha]_D$ .	$[M]_D$ .
0.5376	+1.74°	+32.4°	+98.0°
0.5925	1.99	33.6	99.7

As the molecular rotation of *d*-tartaric acid in the metallic hydrogen tartrates is  $[M]_D + 42^\circ$ , that of the base would be  $[M]_D + 57^\circ$ , a value which agrees very closely with that ( $[M]_D + 60^\circ$ ) previously determined from an examination of the *d*-bromocamphorsulphonates (Tattersall and Kipping, *loc. cit.*).

*l*-Methylhydrindamine Hydrogen Tartrate,  $C_{10}H_{13}N, C_4H_6O_6$ .—This salt crystallises from water in aggregates of small, vitreous, anhydrous prisms, which are readily soluble in water, sparingly so in

\* A 200 mm. tube was used in all the polarimetric observations recorded in this paper.

alcohol, and practically insoluble in chloroform, ethyl acetate, ether, and light petroleum; it melts at  $197^{\circ}$  with slight decomposition. The specific and molecular rotations were determined in aqueous solution with samples dried at  $100^{\circ}$ , 20 c.c. of solution being used.

Weight of salt.	$\alpha_D$ .	$[\alpha]_D$ .	$[M]_D$ .
0.7076	- $0.36^{\circ}$	- $5.0^{\circ}$	- $14.8^{\circ}$
0.6649	0.32	4.8	14.3

In this case, also, the calculated value for the molecular rotation of the *l*-base, namely,  $[M]_D - 56.5^{\circ}$ , agrees closely with that previously deduced from the optical examination of the *d*-bromocamphorsulphonates.

*l*-Methylhydrindamine *d*-Chlorocamphorsulphonate,  
 $C_{10}H_{13}N, C_{10}H_{14}OCl \cdot SO_3H$ .

This salt was prepared in the usual way, the *l*-methylhydrindamine being carefully purified by the crystallisation of its *d*-bromocamphorsulphonate. The product was subjected to prolonged fractional crystallisation from water and separated into eight fractions. At the conclusion of the fractionation, the melting points of the several fractions were determined, those of the first and last fractions being  $239^{\circ}$  and  $231-233^{\circ}$  respectively. The other fractions each melted over a range of  $2-3^{\circ}$ , the values gradually decreasing from the melting point of the first fraction to that of the last. These fractions all crystallised in anhydrous needles resembling the corresponding salt with *d*-bromocamphorsulphonic acid.

The first and last fractions were dried at  $100^{\circ}$  and examined polarimetrically in chloroform and aqueous solutions.

*First Fraction.*

Weight of salt.	Solvent.	Vol. of solution.	$\alpha_D$	$[\alpha]_D^*$	$[M]_D$
I. 0.3496	Chloroform	20 c.c.	+ $0.12^{\circ}$	+ $3.4^{\circ}$	+ $14.0^{\circ}$
II. 0.3351	"	"	0.11	3.28	13.5
I. 0.3496	Water	"	1.19	34.1	140.8
II. 0.3351	"	"	1.15	34.3	141.6

*Last Fraction.*

I.	0.3294	Chloroform	20 c.c.	+ $0.27^{\circ}$	+ $8.2^{\circ}$	+ $33.8^{\circ}$
II.	0.3327	"	"	0.26	7.8	32.2
I.	0.3294	Water	"	1.18	35.8	147.8
II.	0.3327	"	"	1.19	35.8	147.8

It will be noticed that the specific rotations of the last fraction are higher than those of the first both in chloroform and in aqueous solutions. This conclusively proves that the observed difference in rotation cannot be due to any impurity, although the absence of the latter was independently proved, as in all previous experiments. The existence of isomeric salts is therefore established in this case.

*d*-Methylhydrindamine *d*-Chlorocamphorsulphonate,  
 $C_{10}H_{13}N, C_{10}H_{14}OCl \cdot SO_3H$ .

*d*-Methylhydrindamine, purified by the crystallisation of its bromocamphorsulphonate, was combined with *d*-chlorocamphorsulphonic acid, the product subjected to fractional crystallisation from water, and the melting points of the successive fractions determined. The first fraction melted at  $247^\circ$  and the last at  $225-230^\circ$ .

The intermediate fractions had melting points which, extending over a small range, gradually decreased from the melting point of the first fraction to that of the last. These fractions all separated in anhydrous needles resembling the corresponding bromocamphorsulphonate. The first and last fractions were dried at  $100^\circ$  and examined polarimetrically in chloroform and aqueous solutions.

*First Fraction.*

Weight of salt.	Solvent.	Vol. of solution	$\alpha_D$ .	$[\alpha]_D$ .	$[M]_D$ .
I. 0.3912	Chloroform	20 c.c.	+ $2.20^\circ$	+ $56.2^\circ$	+ $231.1^\circ$
II. 0.3953	"	"	2.20	55.7	230.0
I. 0.4049	Water	"	2.44	60.2	248.6
II. 0.4012	"	"	2.41	60.1	248.2

*Last Fraction.*

I. 0.3696	Chloroform	20 c.c.	+ $2.35^\circ$	+ $63.6^\circ$	+ $262.6^\circ$
II. 0.3917	"	"	2.43	62.2	256.8
I. 0.3696	Water	"	2.34	63.4	261.8
II. 0.3917	"	"	2.44	62.4	257.7

In the foregoing tables, numbers I and II indicate different portions of the same sample of material.

The data show that the specific rotations of the last fraction are higher than those of the first, and for the same reasons as in previous cases, these results establish the existence of isomeric salts.

The materials used in this investigation were part of those

previously employed in a former research, and were provided out of a grant made by the Government Grant Committee of the Royal Society.

The author desires to express his thanks to Professor Kipping for the interest he has taken in this research.

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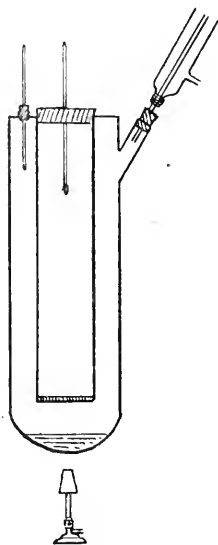
## XXI.—*The Influence of Substitution in the Nucleus on the Rate of Oxidation of the Side-chain. I. Oxidation of the Mono- and Di-chlorotoluenes.*

By JULIUS BEREND COHEN and JAMES MILLER.

ISOLATED observations on the effect of different oxidising agents, and on the influence of certain groups in accelerating or retarding oxidation of the side-chain, have been made by different observers, but the subject has never been systematically investigated. Wroblewsky (*Ber.*, 1882, 15, 1021), without giving experimental details, states that "if benzene with hydrocarbon side-chains in which hydrogen is replaced by a halogen or a nitro-group is submitted to oxidation by chromic acid mixture, those side-chains pass into carboxyl which are farthest from the halogen." Lellmann's *Organische Synthese*, p. 196, contains the following statement: "Negative atomic groups in the ortho-position protect the alkyl group from the action of oxidising agents, whereas alkaline oxidising agents attack this group." The exact reference is not given, but the statement is apparently based on that of Wroblewsky and also on certain observations of W. A. Noyes (*Amer. Chem. J.*, 1885, 7, 145; 1886, 8, 185; 1889, 11, 161). The latter investigator found that *o*-bromotoluene is oxidised with difficulty to *o*-bromobenzoic acid by means of potassium ferricyanide; also that *m*-nitrotoluene is less readily oxidised by this reagent than its isomerides. Schöpff (*Ber.*, 1891, 24, 3778) concludes from the results of his attempts to oxidise *o*-bromo-*m*-xylene that "the oxidation of a methyl group in the ortho-position (to bromine) with acid oxidising agents is effected slowly and with difficulty." Rupp (*Ber.*, 1892, 25, 347) experienced the same difficulty with tetrachloro- and tetrabromo-*p*-xylenes, and only succeeded with a mixture of nitric acid and permanganate. It is clear that no satisfactory generalisation can be drawn from these isolated facts. Certain points which were noticed in the course

of the researches in which one of us has been engaged in collaboration with H. D. Dakin (Trans., 1901, 79, 1111) and with S. H. C. Briggs (Trans., 1903, 83, 1213) on the oxidation of the halogen derivatives of toluene suggested the present inquiry.

The method which we have adopted is to heat about a gram of the substance with dilute nitric acid in a sealed tube for a length of time insufficient for complete oxidation, and to estimate the proportion of acidic product and unchanged substance. In our first experiments, the substance was weighed in small specimen tubes which were slipped into the tube containing the acid. The sealed tubes were heated in a cylindrical, jacketed, tin-plate air-bath which was fixed horizontally, the required temperature being attained by boiling turpentine contained in the outer jacket. The results of the experiments with this apparatus were not concordant. We attributed this partly to the specimen tubes, which to some extent protected the substance from the action of the acid. These tubes were therefore discarded and the substance introduced directly into the acid. We found, moreover, that the inner compartment of the air-bath was about  $5^{\circ}$  hotter at the bottom than at the top, so that the lower tubes were at a higher temperature than the upper ones. The horizontal air-bath was therefore replaced by a vertical one, jacketed as before, and covered with flannel as shown in the figure.



The liquid in the jacket was coal-tar naphtha boiling at  $140\text{--}150^{\circ}$ . Although there was still a difference of about  $3^{\circ}$  between the temperature of the top and bottom of the inner compartment, yet as the tubes, which were approximately of equal length, were placed vertically, they were consequently exposed to the same conditions of temperature.

Care was taken to prevent direct contact between the tubes and the metal of the bath by fixing a cork pad at the bottom and covering the tubes with flannel. Under these modified conditions, concordant results were obtained. The substances employed were the three monochlorotoluenes and the six dichlorotoluenes, all of which were carefully purified by fractional distillation, and in the case of 3:5-dichlorotoluene by crystallisation. The monochlorotoluenes were obtained quite colourless by distillation under diminished pressure, but this treatment was not found necessary in the case of the dichlorotoluenes.

The following are the boiling points of the substances employed:

Monochlorotoluenes.			Dichlorotoluenes.		
	b. p.	mm.		b. p.	b. p.
Ortho-	100°	129	2:3-	200—202°	2:6- 192—194°
Meta-	102	130	2:4-	194·5—195·5	3:4- 203—204
Para-	85	61	2:5-	195—197	3:5- m. p. 26—27

A weighed quantity of the substance (about 1 gram) was introduced into the tube, and about six times this amount of dilute acid (1 vol. nitric acid of sp. gr. 1·4 to 2 vols. water) was added and the tube sealed.

In order to ascertain the effect of the length of the tube on the rate of oxidation, equal quantities of 3:5-dichlorotoluene were heated in two tubes, one of which was about half the length of the other. It was found that the acid formed in the shorter tube was less pure and rather larger in amount, but the difference was insignificant and would be inappreciable in tubes so nearly of the same length as those which we employed.

The air-bath was closed loosely by a cork holding a thermometer and heated until the temperature was constant. The tubes were then introduced, and when the temperature of the inner compartment reached 138—140° the tubes were left for 1½ hours, during which the temperature of the interior did not exceed 145°. The bath was then allowed to cool and the tubes removed and opened. The method of analysis was as follows: the contents of each tube were in turn rinsed into a separating funnel with ether, the contents being then vigorously shaken, whereby the ether dissolved out the whole of the organic compounds. The acid layer was then drawn off and sodium carbonate solution added in excess to the ether and well shaken to extract the organic acid. The alkaline layer was removed and the ethereal extract washed with a small quantity of water, the washings being added to the alkaline liquid. The ethereal solution, which contained the unaltered substance (possibly also a little aldehyde), was dehydrated over calcium chloride, decanted into a tared flask, the ether removed, and the residue weighed. The alkaline liquid was acidified with hydrochloric acid, extracted with ether, the ethereal solution dehydrated over calcium chloride and treated as described above. The purity of the acid was in each case ascertained from the melting point. This and the total quantity of products obtained when compared with the substance taken was a satisfactory check on the result, although, of course, the method lacks the precision of an exact analytical process.

In the following experiments, all the tubes were heated together under precisely the same conditions.

*1st Series.*

Chloro- toluene.	Actual amount taken.	Calculated to 1 gram.			m. p. of acid.	Correct m. p. of acid.
		Chloro- benzoic acid.	Unchanged substance.	Total.		
Ortho-	1·005	1·011	0·040	1·051	135—136°	137°
Meta-	0·989	1·092	0·029	1·121	145—148	153
Para-	0·964	1·058	0·019	1·077	233—234	236
2:3-	1·032	0·942	0·135	1·077	159—162	163
2:4-	1·035	1·073	0·051	1·124	160—161	160
2:5-	1·065	0·864	0·157	1·021	139—142	153
2:6-	1·036	0·825	0·236	1·061	123—132	139—140
3:4-	1·024	1·060	0·047	1·107	200—201	200—201
3:5-	1·046	0·726	0·297	1·023	183—184	182—183
3:5- (short tube)	0·988	0·759	0·228	0·987	184—205	

It will be seen from the above table that the monohalogen compounds are more rapidly attacked than the majority of the dihalogen derivatives, for the former are almost completely converted into acid, whilst only two of the latter are completely oxidised. The dihalogen compounds show well-marked differences; the 3:5-compound is least attacked. The next in order being the 2:5- and 2:6-isomerides, which are oxidised to approximately the same extent, although the 2:6-compound yields a very impure acid. The 2:3-compound comes next, and finally the 2:4- and 3:4-derivatives, which may be bracketed together as being almost completely oxidised.

As the monohalogen compounds were too far oxidised for any conclusions to be drawn as to their relative rates of oxidation, a second experiment was made in which the tubes were heated for only half an hour at 140—145°.

Chloro- toluene.	Amount taken.	Calculated to 1 gram.			m. p. of acid.	Correct m. p. of acid.
		Chloro- benzoic acid.	Unchanged substance.	Total		
Ortho-	1·015	0·687	0·307	0·994	135—136°	137°
Meta-	1·011	0·384	0·548	0·932	146—149	153
Para-	1·007	0·998	0·091	1·089	235—236	236

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It is therefore evident that the meta-compound is least affected, then follows the ortho-derivative, and finally the para-isomeride, which is almost entirely converted into the corresponding chlorobenzoic acid.

Two other series of experiments which were made with the dihalogen compounds confirm the results of the first series.

## 2nd Series.

Dichloro- toluene.	Amount taken.	Calculated to 1 gram.			m. p. of acid.	Correct m. p. of acid.
		Dichloro- benzoic acid.	Unchanged substance.	Total.		
2·3	0·993	0·762	0·290	1·052	159—161°	163°
2·4	0·974	0·949	0·119	1·068	159—159·5	160
2·5	0·989	0·614	0·381	0·995	138—142	153
2·6	1·044	0·546	0·451	0·997	115—129	139—140
3·4	0·997	1·025	0·080	1·105	200—201	200—201
3·5	1·000	0·470	0·495	0·965	183—184	182—183

## 3rd Series.

Chloro- toluene.	Amount taken.	Calculated to 1 gram.			m. p. of acid.	Correct m. p. of acid.
		Dichloro- benzoic acid.	Unchanged substance.	Total.		
2·3	1·076	0·773	0·247	1·020	162—163°	163°
2·4	1·030	1·017	0·096	1·113	160—161	160
2·5	1·165	0·631	0·373	1·004	139—142	153
2·6	1·093	0·640	0·342	0·982	114—128	139—140
3·4	1·165	1·060	0·055	1·115	200—201	200—201
3·5	1·000	0·357	0·581	0·938	182—183	182—183

So far as the special conditions of the above experiments are concerned, namely, the use of halogen compounds on the one hand and of nitric acid as oxidising agent on the other, the results are perfectly definite. The meta-compounds retard oxidation, and the para-compounds assist it, whilst the ortho-compounds occupy an intermediate position. Thus, *m*-chlorotoluene and 3 : 5-dichlorotoluene are least attacked. *p*-Chlorotoluene and the two dichlorotoluenes substituted in the para-position (2 : 4 and 3 : 4) are most readily oxidised. It is not clear why the 2 : 3-dichloro-compound should be more readily

oxidised than the 2:5-derivative, for they are both substituted in the meta- as well as in the ortho-position with respect to the methyl group, nor is it evident why the 2:6- and 2:5-compounds should be oxidised to the same extent. It is interesting to note that Noyes, when working with the nitrotoluenes and potassium ferricyanide, found that the meta-compound is less readily oxidised than the other two isomerides. On the other hand, Wroblewsky's observation (*vide ante*) seems to be only true in part, unless, indeed, chromic acid has a very different action from that of the other two oxidising agents. It is difficult to account for the behaviour of the different isomerides. It is clear that (contrary to the view which we were led to adopt as the result of our preliminary experiments) it is not a question of steric hindrance. The only process which seems to offer any analogy to the present one is that of substitution in the nucleus in which the formation of meta-compounds is sharply differentiated from that of the ortho- and para-compounds, yet it is difficult to see how any process of substitution in the nucleus can be applied to explain the conversion of a side-chain into a carboxyl group. We have accumulated a number of facts in regard to the oxidation of simple and mixed dihalogen derivatives and nitro-halogen compounds of toluene, which we hope shortly to publish.

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## XXII.—*Derivatives of Highly Substituted Anilines.*

By FREDERICK DANIEL CHATTAWAY and JOHN MELLO WADMORE.

A NUMBER of acyl derivatives of the 2:4-dihalogen and the 2:4:6-trihalogen anilines have been prepared during the last few years in the course of an investigation on the phenomena of intramolecular rearrangement in aromatic amines, and their properties are here placed on record.

The anilides can be obtained by heating the substituted aniline with the equivalent amount of propionyl or benzoyl chloride. Vigorous action generally occurs at 160—180°, and the heating is preferably continued so long as hydrogen chloride is evolved. The product can be crystallised from either alcohol or a mixture of chloroform and petroleum. The nitrogen chlorides may all be prepared by adding an excess of a cooled solution of bleaching powder to the anilide dissolved in glacial acetic acid, complete conversion being ensured by extracting with chloroform and vigorously shaking the solution with fresh, slightly

acidified calcium hypochlorite for some hours. The chloroform solution, when dried over calcium chloride and evaporated in a current of dry air, yields the chloroamine derivative in the form of a viscid liquid which at once solidifies on cooling and stirring with light petroleum, and can then be crystallised from petroleum or from a mixture of this solvent with a little chloroform. A pure anilide invariably yields a product which solidifies at once and crystallises readily in lustrous, well-shaped crystals; whereas the presence of even a very small quantity of an admixed isomeride renders the product incapable of solidification. If such a mixture is dissolved in warm petroleum, no crystals form on cooling, but a viscid, semi-solid mass separates, which only occasionally becomes partly crystalline.

*4-Chloro-6-bromobenzanilide*,  $C_6H_3ClBr \cdot NH \cdot CO \cdot C_6H_5$ , separates from alcohol in slender, colourless prisms and melts at  $130.5^\circ$ .

0.2486 yielded 0.2662 mixed AgCl and AgBr. Halogen = 37.30.

$C_{13}H_9ONClBr$  requires halogen = 37.17 per cent.

The percentage of halogen throughout has been calculated on the assumption that silver chloride and silver bromide are present in the precipitate in the same proportion as the respective halogens in the anilide.

*1-Benzoylchloroamino-4-chloro-6-bromobenzene*,  $C_6H_3ClBr \cdot NCl \cdot C_6H_5$ , separated in colourless plates melting at  $62^\circ$ .

0.5084 required 29.2 c.c. *N*/10 I. Cl (as NCl) = 10.18.

$C_{13}H_8ONCl_2Br$  requires Cl (as NCl) = 10.28 per cent.

*4-Chloro-6-bromopropionanilide*,  $C_6H_3ClBr \cdot NH \cdot COEt$ , forms slender, colourless prisms and melts at  $128.5^\circ$ .

0.2332 yielded 0.2947 mixed AgCl and AgBr. Halogen = 44.03.

$C_9H_9ONClBr$  requires halogen = 43.96 per cent.

*2-Chloro-4-bromobenzanilide*,  $C_6H_3ClBr \cdot NH \cdot COPh$ , crystallises from alcohol in transparent, colourless, flattened prisms, and melts at  $145^\circ$ .

0.1868 yielded 0.2007 mixed AgCl and AgBr. Halogen = 37.43.

$C_{13}H_9ONClBr$  requires halogen = 37.17 per cent.

*1-Benzoylchloroamino-2-chloro-4-bromobenzene*,  $C_6H_3ClBr \cdot NCl \cdot COPh$ , forms colourless plates melting at  $74^\circ$ .

0.4224 required 24.7 c.c. *N*/10 I. Cl (as NCl) = 10.36.

$C_{13}H_8ONCl_2Br$  requires Cl (as NCl) = 10.28 per cent.

*2-Chloro-4-bromopropionanilide*,  $C_6H_3ClBr \cdot NH \cdot COEt$ , crystallises in colourless, hair-like needles and melts at  $129^\circ$ .

0.2036 yielded 0.2581 mixed AgCl and AgBr. Halogen = 44.16.

$C_9H_9ONClBr$  requires halogen = 43.96 per cent.

1-Benzoylchloroamino-2 : 4 : 6-tribromobenzene,  $C_6H_2Br_3 \cdot NCl \cdot CPh$ , which separates in glistening, colourless, rhombic plates with domed edges, melts at 115°.

0.2368 required 10 c.c. *N*/10 I. Cl (as NCl) = 7.48.

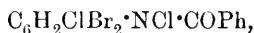
$C_{13}H_7ONClBr_3$  requires Cl (as NCl) = 7.57 per cent.

4-Chloro-2 : 6-dibromobenzanilide,  $C_6H_2ClBr_2 \cdot NH \cdot CPh$ , forms transparent, colourless plates and melts at 194°.

0.2114 yielded 0.2802 mixed AgCl and AgBr. Halogen = 49.88.

$C_{13}H_8ONClBr_2$  requires halogen = 50.16 per cent.

1-Benzoylchloroamino-4-chloro-2 : 6-dibromobenzene,



was obtained in short, colourless, transparent, four-sided prisms with domed ends melting at 111°.

0.2352 required 11.1 c.c. *N*/10 I. Cl (as NCl) = 8.37.

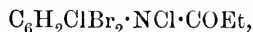
$C_{13}H_7ONCl_2Br_2$  requires Cl (as NCl) = 8.36 per cent.

4-Chloro-2 : 6-dibromopropionanilide,  $C_6H_2ClBr_2 \cdot NH \cdot COEt$ , separates in long, colourless, flattened prisms melting at 185°.

0.2388 yielded 0.3646 mixed AgCl and AgBr. Halogen = 57.45.

$C_9H_8ONClBr_2$  requires halogen = 57.21 per cent.

1-Propionylchloroamino-4-chloro-2 : 6-dibromobenzene,



forms slender, transparent, colourless prisms and melts at 74°.

0.2602 requires 13.7 c.c. *N*/10 I. Cl (as NCl) = 9.33.

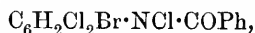
$C_9H_7ONCl_2Br_2$  requires Cl (as NCl) = 9.43 per cent.

2 : 6-Dichloro-4-bromobenzanilide,  $C_6H_2Cl_2Br \cdot NH \cdot CPh$ , crystallises in short, colourless prisms and melts at 195°.

0.2448 yielded 0.3345 mixed AgCl and AgBr. Halogen = 43.43.

$C_{13}H_8ONCl_2Br$  requires halogen = 43.73 per cent.

1-Benzoylchloroamino-2 : 6-dichloro-4-bromobenzene,



forms transparent, colourless plates and melts at 95°.

0.2030 requires 10.7 c.c. *N*/10 I. Cl (as NCl) = 9.34.

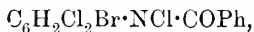
$C_{13}H_7ONCl_3Br$  requires Cl (as NCl) = 9.34 per cent.

2 : 6-Dichloro-4-bromopropionanilide,  $C_6H_2Cl_2Br \cdot NH \cdot COEt$ , crystallises in colourless, flattened prisms melting at  $184^\circ$ .

0.2418 yielded 0.3843 mixed AgCl and AgBr. Halogen = 50.51.

$C_9H_5ONCl_2Br$  requires halogen = 50.80 per cent.

1-Benzoylchloroamino-2 : 4-dichloro-6-bromobenzene,



forms transparent, colourless, four-sided prisms with steeply domed ends and melts at  $92^\circ$ .

0.2204 required 11.7 c.c.  $N/10$  I. Cl (as NCl) = 9.41.

$C_{13}H_7ONCl_3Br$  requires Cl (as NCl) = 9.34 per cent.

2 : 4-Dichloro-6-bromopropionanilide,  $C_6H_2Cl_2Br \cdot NH \cdot COEt$ , crystallises in colourless needles and melts at  $165^\circ$ .

0.2089 yielded 0.3338 mixed AgCl and AgBr. Halogen = 50.78.

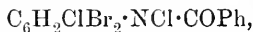
$C_9H_5ONCl_2Br$  requires halogen = 50.80 per cent.

2-Chloro-4 : 6-dibromobenzanilide,  $C_6H_2ClBr_2 \cdot NH \cdot CPh$ , which was obtained in colourless, short prisms terminated by pyramids, melts at  $192^\circ$ .

0.1704 yielded 0.2272 mixed AgCl and AgBr. Halogen = 50.17.

$C_{13}H_5ONClBr_2$  requires halogen = 50.16 per cent.

1-Benzoylchloroamino-2-chloro-4 : 6-dibromobenzene,



separates in colourless, short, four-sided prisms with domed ends and melts at  $97^\circ$ .

0.2240 requires 10.7 c.c.  $N/10$  I. Cl (as NCl) = 8.46.

$C_{13}H_7ONCl_2Br_2$  requires Cl (as NCl) = 8.36 per cent.

2-Chloro-4 : 6-dibromopropionanilide,  $C_6H_2ClBr_2 \cdot NH \cdot COEt$ , forms colourless needles melting at  $185.5^\circ$ .

0.1862 yielded 0.2828 mixed AgCl and AgBr. Halogen = 57.15.

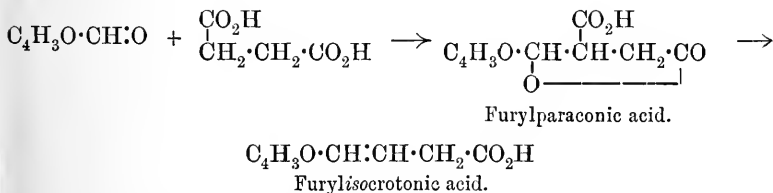
$C_9H_5ONClBr_2$  requires halogen = 57.21 per cent.

XXIII.—*The Condensation of Furfuraldehyde with Sodium Succinate.*

By ARTHUR WALSH TITHERLEY and JAMES FREDERICK SPENCER, B.Sc.

IN the course of an investigation on the higher acids of the succinic series, the authors, in seeking new methods of synthesis, selected furfuraldehyde as a starting point with the intention of converting it into acids of the type  $C_4H_3O \cdot CH:CH \cdot [CH_2]_n \cdot CO_2H$ , and these into suberic acid and its homologues, by processes similar to those by which Baeyer obtained *n*-pimelic acid,  $CO_2H \cdot [CH_2]_5 \cdot CO_2H$ , from furylacrylic acid,  $C_4H_3O \cdot CH:CH \cdot CO_2H$  (*Ber.*, 1877, 10, 695, 1358).

It was anticipated that  $\beta$ -furfurylidene-*propionic* acid (furyl*isocrotonic* acid),  $C_4H_3O \cdot CH:CH \cdot CH_2 \cdot CO_2H$ , the simplest compound of the above type, would be readily formed, according to Fittig's method, by the condensation of furfuraldehyde with sodium succinate in the presence of acetic anhydride (*Annalen*, 1883, 216, 97 ; 1889, 255, 1—142).



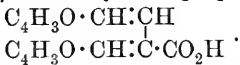
A considerable number of experiments, which have been carried out under a great variety of conditions, show beyond doubt, however, that furfuraldehyde behaves abnormally. Neither furylparaconic acid nor furyl*isocrotonic* acid could be isolated, but two unexpected derivatives,  $C_{13}H_{10}O_4$  and  $C_{14}H_8O_5$ , were obtained, but in such comparatively small yields that their investigation has been attended with considerable difficulty.

In dealing with the two compounds resulting from the condensation, it was at first suspected that the anomalous results might be due to the acetic anhydride having taken part in the reaction, but further investigation disproved this assumption, and it was ultimately shown that one of the products,  $C_{13}H_{10}O_4$ , could be obtained, in the absence of acetic anhydride, by the interaction of furfuraldehyde, sodium succinate, and succinic anhydride.

The compound  $C_{14}H_8O_5$ , which crystallises in long, dark orange-coloured needles melting at  $187^\circ$ , has the properties of a substituted succinic anhydride, and the other,  $C_{13}H_{10}O_4$ , which forms yellow, crystalline plates melting at  $213^\circ$ , was found to be a monobasic acid ; both substances, which are distinctly unsaturated, are produced by the

condensation of 2 molecules of furfuraldehyde with 1 molecule of sodium succinate; the orange-coloured compound being difurfurylidenesuccinic anhydride,

$\text{C}_4\text{H}_3\text{O} \cdot \text{CH} : \text{C} \cdot \text{CO} \begin{array}{c} \diagup \text{O} \\ | \\ \text{C}_4\text{H}_3\text{O} \cdot \text{CH} : \text{C} \cdot \text{CO} \end{array}$ , whilst the yellow compound is  $\alpha\gamma$ -difurfurylidenepropionic acid ( $\alpha$ -furfurylidenefuryliscrotonic acid),

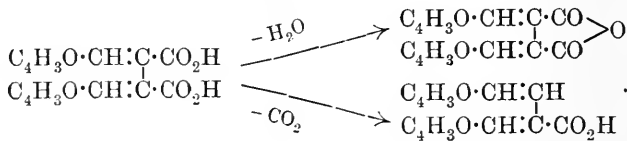


Since the orange-coloured compound is insoluble in cold aqueous alkali hydroxides, whilst the yellow compound dissolves in these solutions, the separation of the two products is readily effected. Unfortunately, their production is accompanied by large quantities of resinous substances having both acid and neutral properties, a fact which renders the purification very tedious.

In spite of a large number of experiments carried out under widely differing conditions, no evidence was obtained of the formation of the monofurfurylidene derivatives. The interaction of furfuraldehyde and sodium succinate in the presence of acetic anhydride may be represented as occurring in the following stages:



The dicarboxylic acid is liberated from the sodium salt by the acetic acid, resulting from the action of the eliminated water on a portion of the acetic anhydride, the excess of the latter reagent then converting the dicarboxylic acid into its anhydride. At the same time, carbon dioxide is removed from another portion of the dicarboxylic acid, giving rise to the monobasic acid:



The final product of the reaction contains, therefore, in addition to a certain amount of the unchanged reagents, the orange-coloured anhydride, the yellow acid and its sodium salt, sodium acetate, acetic and succinic acids, some succinic anhydride,\* and traces of furylacrylic

\* It has been shown beyond question, by separate experiments, that succinic anhydride and sodium acetate are formed when sodium succinate and acetic anhydride are heated together. A double decomposition of this nature was assumed by Fittig and Ott (*Annalen*, 1885, 227, 79) to take place between sodium *isobutyrate* and acetic anhydride, giving rise to *isobutyric* anhydride and sodium acetate, but although the results obtained by these authors could only be interpreted on this assumption, the change was not demonstrated experimentally.

acid. Carbon dioxide is steadily disengaged during the course of the reaction, especially if the temperature is allowed to rise, and whilst the production of yellow acid increases at higher temperatures, that of the orange-coloured anhydride decreases to a corresponding extent.

The succinic anhydride formed as a secondary product in the reaction does not appear to play any special part in the formation of the orange-coloured anhydride, such as might at first be suspected. There can be no doubt that it is the sodium salt alone which enters into action with the aldehyde, as with other condensations of this order (Fittig, *loc. cit.*), for furfuraldehyde could not be made to condense with succinic anhydride in the absence of sodium succinate, either by varying the temperature or by adding acetic anhydride or other dehydrating agents.

Difurfurylidenesuccinic anhydride has a bright scarlet colour resembling that of azobenzene; it is stable towards hydrolytic agents, and is attacked only slowly by boiling aqueous sodium hydroxide, yielding the sodium salt of the corresponding dicarboxylic acid. The acid itself is a pale yellow powder which melts at  $185^{\circ}$ , regenerating the original orange-coloured anhydride. The marked stability of the latter is comparable with that of pyrocinchonic anhydride and the tetra-alkylsuccinic anhydrides, and there can be little doubt that the cyclic structure,  $\begin{array}{c} \text{C} \cdot \text{C} \\ | \quad \diagup \\ \text{C} \cdot \text{C} \end{array} > \text{O}$ , in the orange-coloured compound is more closely allied to the furan nucleus than to the ring present in succinic anhydride. This configuration is, moreover, present in the two furyl groups, and the colour of the compound must in some way be associated with this peculiarity in constitution, and possibly with a special structure in the furan nucleus, having chromogenic characters, like the quinonoid grouping in the benzene nucleus. The chromogenic intensity becomes enhanced when bromine is added to the molecule, and the tetrabromide has marked fluorescent properties (see p. 190).

During this investigation, large quantities of furfuraldehyde were used up in abortive attempts to increase the yields of the yellow and orange-coloured compounds, but although the conditions were varied as far as possible, the yields never exceeded 5 per cent. of the calculated amount, except in one instance when an 8 per cent. yield of the yellow substance was obtained. In many other experiments, traces only were produced.

## EXPERIMENTAL.

*Action of Furfuraldehyde on Sodium Succinate in presence of Acetic Anhydride. Formation and Separation of Difurfurylidene-succinic Anhydride and  $\alpha$ -Difurfurylidene-propionic Acid.*

An intimate mixture of furfuraldehyde, thoroughly dried sodium succinate, and freshly distilled acetic anhydride, contained in a flask fitted with an air condenser, was cautiously heated in a paraffin-bath. The reaction commenced at 100° and proceeded so vigorously above this temperature that occasionally, when large quantities were employed, it became uncontrollable, and gave rise to black, resinous products. The most favourable yields were obtained by heating together at 90—100° for 6 hours, 20 grams of furfuraldehyde, 30 grams of sodium succinate and 45 grams of acetic anhydride. It was found necessary to employ the sodium salt in the form of a very fine powder, which was dried at 140° just before the experiment.

During the condensation, small quantities of carbon dioxide were evolved and the contents of the flask darkened, the final semi-solid product having a dark greenish-brown colour. The relative proportion of orange-coloured anhydride and yellow acid produced varied considerably with the conditions (time and temperature), but in general the yellow acid increased at the expense of the anhydride if the temperature was allowed to rise above 100° and if the heating continued for more than 6 hours, whilst in many cases under these circumstances the anhydride was not isolated. It was, moreover, impossible to obtain the anhydride exclusively by working at lower temperatures. These two products were isolated and separated by one or other of the following methods.

1. *Ether Extraction.*—The contents of the flask were treated with ether, and the solid residue, after filtering, further extracted in a Soxhlet apparatus for 4 or 5 hours, this treatment being necessary owing to the sparing solubility of the yellow and orange-coloured substances in ether. The dark ethereal extracts, on evaporation, slowly yielded these two compounds, together with succinic acid and succinic anhydride, the mother liquor containing acetic acid and its anhydride, furfuraldehyde and resin. The crystals, which were much discoloured, assumed a bright orange colour after draining on a porous plate. They were now treated with dilute ammonia, in which the orange-coloured anhydride remained undissolved as a granular powder. This product was purified by recrystallising from hot glacial acetic acid, and finally from hot benzene. The highest yield of difurfurylidene-succinic anhydride thus obtained, after about thirty separate syntheses

had been carried out in order to ascertain the best conditions of treatment, was about 5 per cent. of the calculated amount.

In order to isolate the yellow acid ( $\alpha\gamma$ -difurfurylidenepropionic acid) which accompanies the anhydride, the ammoniacal filtrate from the latter was acidified with hydrochloric acid. A dirty yellowish-brown precipitate of the impure acid was deposited, which was found to be very difficult to purify, owing to the presence of brown, oily resins having an acid nature, these substances were also precipitated, and rendered it almost impossible to dry the product. When gently warmed, the impure material melted to a black tar, which could not be effectually purified. By repeated crystallisation of the dried precipitate from hot benzene, however, it was at length found possible to separate the less fusible, yellow, crystalline acid in a fairly pure condition from the oily resins.

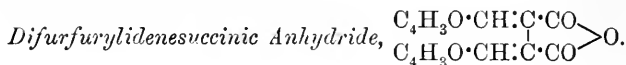
An alternative, and much more satisfactory method of purification was ultimately devised, depending on the fact that the sodium salt of the yellow acid is not very soluble in water and crystallises readily, whilst the sodium salts of the impurities are more soluble and do not crystallise. The impure product, obtained by acidifying the above ammoniacal solution, was therefore washed, dissolved in a slight excess of sodium hydroxide solution, and the resulting dark brown solution of the sodium salts concentrated carefully on the water-bath until crystals commenced to separate. On cooling, the entire mass became crystalline, and the sodium salt, when collected at the pump and dried on a porous plate, was obtained in large, transparent, orange-yellow plates. The mother liquor generally yielded a second crop of crystals.

The  $\alpha\gamma$ -difurfurylidenepropionic acid obtained from this sodium salt by the action of hydrochloric acid was absolutely pure and melted  $5^{\circ}$  higher than that obtained by the foregoing method of crystallisation from benzene. The maximum yield was about 5.5 per cent. of theory, this being obtained only by carrying out the original reaction at  $110^{\circ}$ , so as to diminish the production of the orange-coloured compound.

2. *Treatment with Water.*—A method of treatment similar to that employed by Fittig (*loc. cit.*) was adopted by the authors in a number of experiments made in endeavouring to isolate furylparaconic and furylisocrotonic acids. These acids could, however, not be detected. The steam distillate contained only furfuraldehyde; the residue in the flask contained a large quantity of oily resin, which was filtered off whilst hot. The filtrate was yellow, and on cooling became turbid, and in the course of two to three days a bright yellow, micro-crystalline powder appeared in the form of crusts on the surface of the liquid and sides of the vessel; this substance melted at about  $200^{\circ}$ , and was fairly pure  $\alpha\gamma$ -difurfurylidenepropionic acid. It was crystallised

repeatedly from benzene. The aqueous filtrate from the yellow crusts contained only acetic acid, succinic acids, and their sodium salts.

The tarry matter was also examined, and, although it was found to contain a relatively considerable proportion of the yellow  $\alpha\gamma$ -difurfurylidene- $\beta$ -propiolic acid (which was extracted by repeated treatment with hot water, in which this acid is appreciably soluble), no other acid, except the resin acids, could be obtained from it. The quantity of tarry matter or pitch obtained in all the experiments was very great, and at once explained the very small yields, but it was impossible under any conditions to prevent its formation, although by carefully regulating the temperature at which the condensation was effected its quantity could be more or less minimised. The resin was closely investigated and, by repeated solution in alkali and reprecipitation with acids, was obtained in the form of a brown, amorphous powder, which was distinctly unsaturated, had slightly acid characters, and exhibited properties analogous to the yellow, crystalline  $\alpha\gamma$ -difurfurylidene- $\beta$ -propiolic acid. It had, however, no definite melting point, and evidently consisted of a mixture of several substances (probably polymerised derivatives), and, although numerous attempts were made to separate them by means of solvents, definitely pure compounds could not be isolated. The mixture was instantly oxidised by cold potassium permanganate, giving large quantities of oxalic acid. This investigation was accordingly abandoned.



This acid crystallises in fine, silky needles from benzene, but forms thick prisms when separating slowly from glacial acetic acid; it melts at  $187^\circ$ .

0.1123 gave 0.2684  $\text{CO}_2$  and 0.0351  $\text{H}_2\text{O}$ .  $\text{C} = 65.18$ ;  $\text{H} = 3.47$ .

0.0872 „ 0.2080  $\text{CO}_2$  „ 0.0270  $\text{H}_2\text{O}$ .  $\text{C} = 65.05$ ;  $\text{H} = 3.43$ .

$\text{C}_{14}\text{H}_8\text{O}_5$  requires  $\text{C} = 65.62$ ;  $\text{H} = 3.12$  per cent.

A determination of its molecular weight was carried out by the ebullioscopic method in benzene solution.

	Solute.	Solvent.	Rise of b. p.	M. W.
I.	0.1524	34.168	0.045	264
II.	0.2926	34.168	0.090	254

$\text{C}_{14}\text{H}_8\text{O}_5$  requires M. W. = 256.

Difurfurylidenesuccinic anhydride is only very sparingly soluble in the usual organic solvents, but the solutions have a bright orange colour. In benzene, it is fairly readily soluble in the hot, but only slightly so in the cold solvent (1 part in 350 at  $14^\circ$ ).

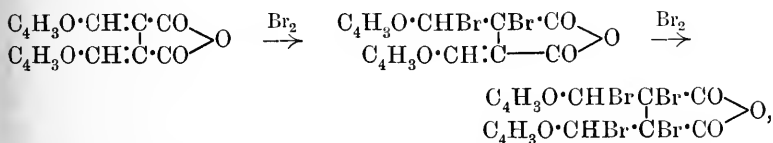
It is insoluble in and unaffected by water, aqueous sodium carbonate, ammonia, &c.; also by cold aqueous sodium hydroxide, but in a boiling solution of this alkali it is slowly attacked and disappears, forming a pale yellow solution of the sodium salt of the corresponding dicarboxylic acid.

Attempts made to reduce difurfurylidenesuccinic anhydride by zinc dust and glacial acetic acid, and other reducing agents gave no satisfactory results, mainly owing to insufficiency of material.

On cautiously oxidising the substance with nitric acid, potassium permanganate, or chromic acid, oxalic acid was formed, this result being due to the presence of the furan nucleus. An appreciable quantity of a syrupy acid was simultaneously formed, but this substance could not be purified or identified owing to its small amount.

*Action of Bromine on Difurfurylidenesuccinic Anhydride.*

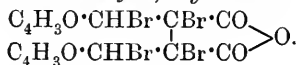
Owing to the markedly unsaturated character of the anhydride and the presence of two furyl groups, bromine interacts with great vigour and its chloroform solution is instantly decolorised. It is probable that the first action consists in adding two and then four atoms of the halogen at the points of double union outside the furyl groups thus :



further addition then taking place in the furan nucleus. The action is further complicated by the fact that substitution simultaneously occurs, with evolution of hydrogen bromide and formation of viscous bromo-derivatives. When, however, the bromine is carefully added, comparatively little substitution occurs until four atoms of bromine have been introduced. Experiments were then made with the view of introducing bromine in successive stages corresponding with 2, 4, 6, and more atoms. A saturated solution of the orange-coloured anhydride in chloroform was treated with the requisite volume of a solution of bromine in the same solvent added drop by drop; the solvent was then allowed to evaporate and the residue purified. It was found impossible to isolate in a pure condition any product other than the tetrabromide. In the experiments in which two atoms of bromine only had been added, a mixture of granular and viscous substances remained which were found to contain the tetrabromide and unchanged difurfurylidenesuccinic anhydride, but no dibromide. From those experiments, also, in which an excess of

bromine had been used, the chief product isolated was the tetrabromide, the remainder being a syrupy mixture from which no definite substance could be isolated.

$\alpha\alpha_1\beta\beta_1$ -Tetrabromo-s-difurfurylsuccinic Anhydride,



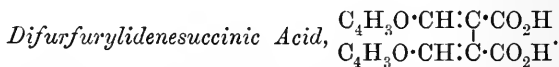
This compound was obtained in largest quantity by the addition of four atoms of bromine to difurfurylidenesuccinic anhydride. The residue, after removing the chloroform, had a brown, vitreous appearance; it was washed several times with cold alcohol and recrystallised from benzene, being then obtained in micro-crystalline, yellow needles melting at 195—196°.

0.1736 gave 0.2270 AgBr. Br = 55.16.

$\text{C}_{14}\text{H}_8\text{O}_5\text{Br}_4$  requires Br = 55.55 per cent.

The tetrabromo-derivative is fairly readily soluble in chloroform, benzene or acetone, but only sparingly so in alcohol; its solutions have a yellow fluorescence, which is destroyed by alkalis and restored by acids.

An attempt was made to obtain the dibromo-derivative by using glacial acetic acid as a solvent for the bromine. On adding water to the product of reaction, a yellow powder was deposited, which, when dissolved in acetic acid and reprecipitated with water, melted indefinitely at about 112° and contained 33.46 per cent. of bromine. The dibromide,  $\text{C}_{14}\text{H}_8\text{O}_5\text{Br}_2$ , requires Br = 38.46 per cent. By further treatment with acetic acid and water, it was obtained apparently pure, and melted at 135°, but unfortunately the quantity was too small for analysis.



The orange-coloured anhydride was digested with about twice the theoretical quantity of a 30 per cent. solution of pure sodium hydroxide in a silver vessel at 100° for several hours until the last traces of orange-coloured needles had disappeared. A slightly yellow solution resulted, which, after cooling, was acidified with hydrochloric acid. A pale yellow, crystalline precipitate was gradually deposited, the total yield being theoretical. The acid was purified by dissolving in aqueous sodium carbonate and reprecipitating with acid. The pure substance melted at 185—187°, but at 185° it rapidly assumed a deep orange colour and then melted to a blood-red liquid, evolving steam and yielding the anhydride (m. p. 187°).

0.0724 gave 0.1639  $\text{CO}_2$  and 0.0244  $\text{H}_2\text{O}$ .  $\text{C} = 61.73$ ;  $\text{H} = 3.74$ .

$\text{C}_{14}\text{H}_{10}\text{O}_6$  requires  $\text{C} = 61.31$ ;  $\text{H} = 3.64$  per cent.

The acid is fairly readily soluble in alcohol and acetone; it dissolves very easily in glacial acetic acid, but is insoluble in benzene and chloroform. It forms a yellow, crystalline sodium salt and a bright yellow, insoluble silver salt.

When the acid is warmed with acetyl chloride, it dissolves, and the colour of the solution rapidly changes from yellow to blood-red, then almost instantaneously the pure anhydride separates as a net-work of bright orange-coloured needles melting at  $187^\circ$ .

*$\alpha\gamma$ -Difurfurylidene- $\beta$ -propionic Acid ( $\alpha$ -Furfurylidene-furylisocrotonic Acid),*  
 $\text{C}_4\text{H}_3\text{O} \cdot \text{CH} : \text{CH}$   
 $\text{C}_4\text{H}_3\text{O} \cdot \text{CH} : \dot{\text{C}} \cdot \text{CO}_2\text{H} \cdot$

The isolation of this compound from the product of interaction of furfuraldehyde, sodium succinate, and acetic anhydride has already been described. An 8 per cent. yield of this acid was obtained by using succinic anhydride as dehydrating agent instead of acetic anhydride. By this method, the formation of difurfurylidene-succinic anhydride was prevented. The use of large quantities was avoided, the preparation being carried out on a small scale. Eight grams of sodium succinate (dried at  $140^\circ$ ), 6 grams of succinic anhydride, and 5 grams of furfuraldehyde were intimately mixed and heated at  $120^\circ$  in a paraffin bath for 4—5 hours. The solid product, which had darkened considerably, was pulverised in a mortar and digested with aqueous sodium carbonate at  $40^\circ$  for about 2 hours. A considerable quantity of brown, insoluble, resinous matter remained, which was filtered off, and the yellow solution, after cooling, acidified with hydrochloric acid. The yellow precipitate, which was somewhat oily, was washed thoroughly and purified by conversion into its sodium salt (compare p. 187), the acid being subsequently liberated by treatment with hydrochloric acid. The purest specimen of the acid obtained in this manner melted at  $213^\circ$ . A number of specimens in the earlier experiments, which had been purified by recrystallisation from benzene and other solvents, melted at  $205^\circ$ , evidently owing to traces of adherent resinous matter.

m. p.  $205^\circ$ . 0.1096 gave 0.2702  $\text{CO}_2$  and 0.0423  $\text{H}_2\text{O}$ .  $\text{C} = 67.23$ ;  $\text{H} = 4.28$ .

m. p.  $205^\circ$ . 0.1858 gave 0.4569  $\text{CO}_2$  and 0.0732  $\text{H}_2\text{O}$ .  $\text{C} = 67.21$ ;  $\text{H} = 4.39$ .

m. p.  $213^\circ$ . 0.2169 gave 0.5419  $\text{CO}_2$  and 0.0865  $\text{H}_2\text{O}$ .  $\text{C} = 68.07$ ;  $\text{H} = 4.43$ .

$\text{C}_{13}\text{H}_{10}\text{O}_4$  requires  $\text{C} = 67.33$ ;  $\text{H} = 4.34$  per cent.

$\alpha\gamma$ -Difurfurylidene- $\beta$ -propiolic acid is practically insoluble in water, slightly soluble in ether, cold alcohol or benzene, but may be crystallised from its hot solution in the last two solvents in long, yellow needles; it is readily soluble in glacial acetic acid, and is reprecipitated by water as a bright yellow precipitate. The acid at once dissolves in aqueous alkali hydroxides, including ammonia, and is slowly soluble in sodium carbonate solution, being reprecipitated from these solutions by mineral acids or acetic acid.

The *sodium* salt is sparingly soluble in water and crystallises in large, transparent, orange-yellow plates, which at  $100^\circ$  lose water and crumble to an opaque, bright yellow powder.

The *silver* salt is precipitated from neutral solutions on adding silver nitrate as a bright yellow, colloidal precipitate.

0.0720 gave 0.0232 Ag.  $\text{Ag} = 32.22$ .

$\text{C}_{13}\text{H}_9\text{O}_4\text{Ag}$  requires  $\text{Ag} = 32.05$  per cent.

In pure water, the salt is fairly soluble, forming a pale yellow solution.

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## XXIV.—*The Constitution of Epinephrine.*

By HOOPER ALBERT DICKINSON JOWETT.

"EPINEPHRIN," the name given by Abel and Crawford to the active principle of the suprarenal gland, was first isolated by them in an impure condition in 1897 (Johns Hopkins Hospital Bulletin, No. 76), and a similar substance, also more or less impure, but prepared by a different method, was obtained by von Fürth (*Zeit. physiol. Chem.*, 1900, 29, 105), who called it "suprarenin."

In 1901, the active principle was isolated in a crystalline condition by Takamine (*Amer. J. Pharm.*, 1901, 73, 523) and called by him "adrenalin," and shortly afterwards it was prepared by a different method by Aldrich (*Amer. J. Physiol.*, 1901, 5, 457).

The three names "epinephrin," "suprarenin," and "adrenalin," therefore refer to the same substance, although Abel (*Ber.*, 1903, 36, 1839) has since adopted the term "epinephrin hydrate." As this author was the first to isolate the substance, although in an impure condition, it would seem that the name originally assigned by Abel to the active principle should be the one adopted. Takamine, from the results of analyses of crystalline epinephrine, proposed the formula

$C_{10}H_{15}O_3N$ , and showed that, although it acted as a mono-acidic base, it gave no reaction with the usual alkaloidal reagents. Aldrich, however, preferred the slightly different formula  $C_9H_{13}O_3N$ .

Abel, who carefully purified his material, adopted the formula  $C_{10}H_{13}O_3N, \frac{1}{2}H_2O$ , but adduced absolutely no evidence to show that it contained any water of crystallisation. His results agree equally well with Aldrich's formula  $C_9H_{13}O_3N$ . This is seen from the following numbers calculated for each formula :

(Aldrich's formula)  $C_9H_{13}O_3N$  requires C = 59.0 ; H = 7.1 ; N = 7.6.

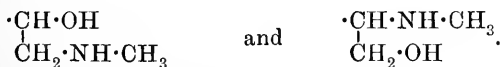
(Abel's formula)  $C_{10}H_{13}O_3N, \frac{1}{2}H_2O$  requires C = 58.8 ; H = 6.9 ; N = 6.9.

Abel actually found C = 58.4 to 58.7 ; H = 6.8 to 7.2 ; N = 7.1 to 7.6 per cent.

Von Fürth (*Monatsh.*, 1903, 24, 261) confirmed the formula  $C_9H_{13}O_3N$  by analyses and molecular weight determinations.

Pauly (*Ber.*, 1903, 36, 2945), from the results of the analysis of very carefully purified material, also confirmed this formula, so that it must be considered the most probable of those proposed. No crystalline salts or derivatives have been described, but von Fürth prepared a tribenzoyl- and a tribenzenesulpho-derivative. He also showed that it contained no methoxyl group, and that it yielded methylamine by treatment with concentrated acids.

Of the degradation products of epinephrine, only protocatechuic acid, formed by fusion with potassium hydroxide, has been positively identified, although substances giving the pyrrole, skatole, or catechol reactions have been obtained by different observers. Von Fürth suggested for the base the partially developed formula  $[CH_3 \cdot NC_2H \cdot OH]C_6H_6(OH)_2$ , and Pauly, who determined its specific rotation, suggested that it contained a hydroxylated benzene residue attached to one of five possible complexes, of which the most probable were the following :



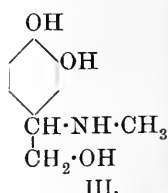
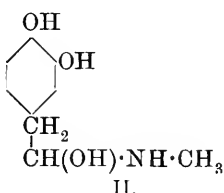
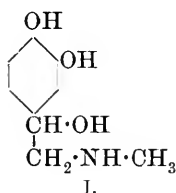
In this way, the formation of catechol, skatole, or pyrrole derivatives would be easily explained.

In the present investigation, I have confirmed the formula  $C_9H_{13}O_3N$ , first proposed by Aldrich, by analyses of carefully purified material and by molecular weight determinations. By fusion with potassium hydroxide, a small quantity of a crystalline substance giving the reactions of protocatechuic acid was isolated, but the amount was so small that it was doubtful whether the presence of this complex in the original substance could be correctly deduced from its formation.

By oxidation with permanganate, oxalic and formic acids and methylamine were obtained.

By methylation and subsequent oxidation with permanganate, trimethylamine and veratric acid were obtained, thus proving the existence of the complexes  $C_6H_3(OH)_2 \cdot C$  and  $NH(CH_3)$  in the original base.

From these results, the following constitutional formulæ of epinephrine may be deduced :



Of these formulæ, I is the more probable, for if II were correct, then, after methylation and subsequent oxidation, we should expect the product to yield homoveratric acid,  $C_6H_3(OH)_2 \cdot CH_2 \cdot CO_2H$ , whereas veratric acid was actually obtained, whilst III would not so readily explain the formation of pyrrole or skatole derivatives. Formula I may therefore be considered to represent correctly the constitution of epinephrine, and it serves to explain the ordinary reactions of the base as well as the formation of pyrrole, skatole, or catechol derivatives as degradation products.

## EXPERIMENTAL.

### *The Formula and Properties of Epinephrine.*

The crude crystalline material was first freed from inorganic impurities by the method previously adopted by other observers, namely, solution of a salt in alcohol and fractional precipitation with ether. It was finally purified by fractional precipitation of the base from the aqueous solution of its hydrochloride by ammonia.

The analyses of four different specimens were sufficient to confirm the formula  $C_9H_{13}O_3N$ .

0.1184 gave 0.2546  $CO_2$  and 0.0798  $H_2O$ .  $C = 58.6$  ;  $H = 7.5$ .

0.1082 „ 0.2306  $CO_2$  „ 0.0720  $H_2O$ .  $C = 58.1$  ;  $H = 7.4$ .

0.1238 „ 0.2642  $CO_2$  „ 0.0816  $H_2O$ .  $C = 58.2$  ;  $H = 7.3$ .

0.0990 „ 0.2136  $CO_2$  „ 0.0644  $H_2O$ .  $C = 58.8$  ;  $H = 7.2$ .

0.1342 „ 9.2 c.c. N at  $15^\circ$  and 755 mm.  $N = 7.8$ .

0.0946 in 24.78 glacial acetic acid gave  $\Delta t - 0.11^\circ$ . M. W. = 135.

$C_9H_{13}O_3N$  requires  $C = 59.0$  ;  $H = 7.1$  ;  $N = 7.6$  per cent. M. W. = 183.

The determination of the specific rotation of the base in dilute acetic acid solution gave the following result :

$$\alpha_D = -10'; l = 0.25 \text{ dcm.}; c = 2.084; [\alpha]_D = -32.0^\circ.$$

Pauly (*loc. cit.*) found  $[\alpha]_D -43^\circ$ , but considering the small observed angle ( $10'$ ) the above figures do not vary beyond the limits of experimental error.

The general statements of previous observers as to the solubility of epinephrine in various solvents and its behaviour towards alkaloidal reagents were confirmed. The base did not react with phenylhydrazine.

#### *Oxidation with Permanganate.*

Five grams of epinephrine were dissolved in dilute sulphuric acid and oxidised at the ordinary temperature with a 1 per cent. solution of permanganate, 30 grams of this reagent being required to produce a permanent colour. The product yielded methylamine, which was identified by its platinichloride.

0.1646 gave 0.0688 Pt.  $\text{Pt} = 41.8$ .

$(\text{CH}_5\text{N})_2, \text{H}_2\text{PtCl}_6$  requires  $\text{Pt} = 41.3$  per cent.

The acids obtained were formic and oxalic acids.

#### *Fusion with Potassium Hydroxide.*

Five grams of epinephrine were added to 25 grams of potassium hydroxide and the mass fused at as low a temperature as possible. The melt was then dissolved in water, acidified, and extracted with ether. The residue, after distilling off the ether, was obtained crystalline and gave the characteristic protocatechuic acid reaction on adding successively ferric chloride and sodium carbonate. The amount obtained was insufficient to admit of further examination.

#### *Methylation and Subsequent Oxidation with Permanganate.*

Four grams of epinephrine were dissolved in 50 c.c. of methyl alcohol in which 1 gram of sodium had been dissolved, and 8 grams of methyl iodide added. The mixture was then heated in a sealed tube at  $100^\circ$  for four hours, the alcohol distilled off, and the operation repeated with the residue. After the second methylation, the residue was dissolved in water and then added to an aqueous solution of 17 grams of silver nitrate, the silver iodide quickly filtered off, and the filtrate saturated with hydrogen sulphide and again filtered. The filtrate was then oxidised with a 2 per cent. solution of perman-

ganate at the ordinary temperature, when 10 grams were required to produce a permanent colour. The product, when worked up in the usual way, yielded a volatile base which was identified as trimethylamine.

0.1588 Pt salt gave 0.059 Pt. Pt = 37.1.

$(C_3H_9N)_2 \cdot H_2PtCl_6$  requires Pt = 37.1 per cent.

The crystalline acid obtained from the ethereal extract was recrystallised from hot water until its melting point was constant; it formed white, acicular crystals, sparingly soluble in cold water and melting sharply at  $179^\circ$ . The aqueous solution gave no reaction with ferric chloride.

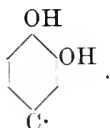
0.1128, dried at  $110-120^\circ$ , gave 0.2446  $CO_2$  and 0.057  $H_2O$ . C = 59.1 H = 5.6.

$C_9H_{10}O_4$  requires C = 59.3; H = 5.5 per cent.

This compound was therefore identified as veratric acid.

#### *The Constitution of Epinephrine.*

Since the product obtained by exhaustive methylation yields veratric acid by oxidation with permanganate, epinephrine must contain the complex :



As it yields trimethylamine by the foregoing treatment and methylamine by oxidation of the original base, it must therefore contain the group  $\cdot NH(CH_3)$ , which, being split off by simple oxidation, is most probably attached to the side-chain and not to the benzene nucleus.

As epinephrine yields tribenzoyl- and tribenzenesulpho-derivatives, it probably contains three hydroxyl groups, of which two are attached to the benzene nucleus.

The only probable formulæ which would comply with the above conditions and also conform to Pauly's hypothesis (*loc. cit.*) are those indicated on p. 194.

Of these, I is the most probable, for if II were correct we should expect after methylation and subsequent oxidation to obtain homoveratric acid and not veratric acid. Moreover, III would not so readily explain the formation of pyrrole or skatole derivatives.

Formula I is therefore the most probable formula for epinephrine, as by it the formation of catechol or protocatechuic acid is easily explained

as well as the reducing properties of the base. It also contains one of the two side-chains regarded as probable by Panly (*loc. cit.*). By the union of the nitrogen atom to the benzene ring, pyrrole derivatives would be formed, as has been stated to be the case.

*Addendum.*—Since this paper was written, a communication by Abel has appeared (*Ber.*, 1904, 37, 368) in which he still adheres to the formula  $C_{10}H_{13}O_3N, \frac{1}{2}H_2O$ . He states, however (*loc. cit.*, 381), that 0.2288 gram of the base, when heated for one hour at  $145^\circ$  and subsequently for one hour at  $155$ – $160^\circ$  in a vacuum, lost only 0.0014 gram or 0.6 per cent. This experiment apparently only affords further evidence that the base contains no water of crystallisation.

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## XXV.—*The Resolution of $\alpha\beta$ -Dihydroxybutyric Acid into its Optically Active Constituents.*

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THE two inactive  $\alpha\beta$ -dihydroxybutyric acids, obtained by Fittig and Kochs on oxidising the  $\alpha$ - and  $\beta$ -crotonic acids with barium permanganate (*Annalen*, 1892, 268, 8 and 16), are characterised mainly by the different solubilities of their salts in water. If the  $\alpha$ - and

$\beta$ -crotonic acids are represented by the formulæ  $\overset{\text{H}}{\text{CH}_3} \cdot \overset{\text{H}}{\text{C}} = \overset{\text{H}}{\text{C}} \cdot \text{CO}_2\text{H}$  and

$\overset{\text{H}}{\text{CH}_3} \cdot \text{C} = \overset{\text{H}}{\text{C}} \cdot \text{CO}_2\text{H}$ , the two  $\alpha\beta$ -dihydroxybutyric acids ( $\beta$ -methyl-

glyceric and  $\beta$ -methylisoglyceric acids) should have the formulæ

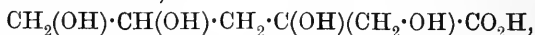
$\overset{\text{H}}{\text{CH}_3} \cdot \overset{\text{H}}{\text{C}} - \overset{\text{H}}{\text{C}} \cdot \text{CO}_2\text{H}$  and  $\overset{\text{HO}}{\text{CH}_3} \cdot \overset{\text{H}}{\text{C}} - \overset{\text{OH}}{\text{C}} \cdot \text{CO}_2\text{H}$ .

In connection with an investigation on the oxidation of carbohydrates which is being carried out by one of us, it seemed advisable to investigate the properties of these acids more completely and to prepare their salts with optically active bases, with the view of resolving the racemic forms into their optically active components.

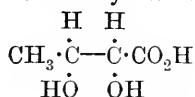
In this paper, we communicate the results of an investigation of the properties of the *l*-modification of  $\alpha\beta$ -dihydroxybutyric acid and of one of the salts of the *d*-modification. In the course of our investigation, we were led to believe that a more complete separation of  $\beta$ -crotonic acid from  $\alpha$ -crotonic acid could be effected, but this portion of the work will form the subject of another paper. The resolution of  $\beta$ -methylglyceric acid can be easily effected by the fractional crystallisation of the quinidine salts. The quinidine *l*- $\beta$ -methylglycerate is sparingly soluble in water and yields the *l*-acid, having a specific rotation of  $-13.5^\circ$ . The barium *l*-salt is more strongly lævoptatory,  $[\alpha]_D -20^\circ$ , and the rotation of this salt is greater than that of calcium glycerate ( $-11.66^\circ$ ), derived from *d*-glyceric acid, which has  $[\alpha]_D^{127} +2.14^\circ$ ; moreover, the rotation of barium *l*- $\beta$ -methylglycerate has the same sign as that of the acid (compare Frankland and Frew, Trans., 1891, 59, 56, 101).

The specific rotation of an aqueous solution of  $\alpha\beta$ -dihydroxybutyric acid is unchanged when allowed to remain for 12 hours, and since it is slightly lower than that of the barium salt there is probably no anhydride present in the solution. In the case of *d*-glyceric acid, there is evidence of the formation of an anhydride on the evaporation of an aqueous solution (Frankland and Frew, Trans., 1891, 59, 56). Comparison with the specific rotation of *l*- $\beta$ -hydroxybutyric acid shows that the introduction of a hydroxyl group lowers the rotation of the acid. The specific rotation of *l*- $\beta$ -hydroxybutyric acid is  $[\alpha]_D -24.8^\circ$ , whilst that of the corresponding sodium salt is  $[\alpha]_D -14.5^\circ$  (Mackenzie, Trans., 1902, 81, 1402). Mackenzie states that the rotations of  $\beta$ -hydroxybutyric acid and its salts are exceptional, in that the salts have lower rotations than that of the free acid. An aqueous solution of  $\beta$ -hydroxybutyric acid contains some anhydride, but the rotation of the anhydride differs very little from that of the free acid (*loc. cit.*)

By the action of lime water on an oxycellulose, Faber and Tollens obtained isosaccharic acid,



and a dihydroxybutyric acid. This dihydroxybutyric acid was found to have a specific rotation  $[\alpha]_D -2.6^\circ$ , in freshly prepared aqueous solution, but after three days the specific rotation had changed to  $+13.7^\circ$  (*loc. cit.*). The acid is probably the optical isomeride of the *l*- $\alpha\beta$ -hydroxybutyric acid obtained by us. The formula



rather than  $\text{CH}_2(\text{OH})\text{CH}_3 > \text{C}(\text{OH})\cdot\text{CO}_2\text{H}$ , ought to be assigned to Faber

and Tollens's acid. The optical isomerism of these two acids perhaps might be considered as affording some slight evidence in favour of the existence of a methylpentose residue in cellulose. The oxycelluloses are characterised in certain cases by the presence of active carbonyl groups, by methoxyl radicles, and by yielding furfuraldehyde as a product of acid hydrolysis (Cross and Bevan, *Cellulose*, p. 82). The production of furfuraldehyde indicates generally the presence of a pentose nucleus, although it may also be obtained from glycuronic acid and glucosone, which are derived from hexoses.

### EXPERIMENTAL.

$\beta$ -Methylglyceric acid, which was prepared from solid crotonic acid by oxidation with barium permanganate according to the directions given by Fittig and Kochs (*loc. cit.*), was converted into its salts with brucine, quinine, strychnine, morphine, and quinidine.

*Brucine  $\beta$ -Methylglycerate.*—This salt is exceedingly soluble in water and fairly soluble in hot absolute alcohol, one part of the salt dissolving in 15 parts of the boiling solvent; it crystallises from a concentrated alcoholic solution in small needles, but if the solution is more dilute, nodular aggregates of needles slowly separate. It melts at  $236^\circ$  with decomposition.

0.2012 gave 9.8 c.c. moist nitrogen at  $22^\circ$  and 765 mm.  $N = 5.58$ .

$C_{23}H_{26}O_4N_2, C_4H_8O_4$  requires  $N = 5.45$  per cent.

The specific rotation of the salt was determined in both alcohol and water.

(1) In alcohol:  $l = 1$ ;  $c = 1.333$ ;  $\alpha_D^{20} - 0.2^\circ$ ;  $[\alpha]_D^{20} - 15^\circ$ .

(2) In water:

$l = 1$ ;  $c = 9.983$ ;  $d = 1.026$ ;  $\alpha_D^{16} - 2.88^\circ$ ;  $[\alpha]_D^{16} - 28.12^\circ$ .

Tykociner found that the specific rotation of a brucine salt of an inactive acid dissolved in water was approximately  $-34^\circ$ . The brucine salt is apparently that of the inactive acid (*Rec. trav. chim.*, 1892, 11, 148). Fractional crystallisation of the salt failed to alter its rotation appreciably, and a determination of the specific rotatory power of the last crop of crystals from the aqueous solution gave the following numbers:

$l = 1$ ;  $c = 10.123$ ;  $d = 1.0277$ ;  $\alpha_D^{16} - 2.89^\circ$ ;  $[\alpha]_D^{16} - 27.8^\circ$ .

The acid was produced by decomposing successively the brucine salt by baryta and the barium salt by the exact amount of sulphuric acid; it crystallised from a mixture of dry acetone and dry ether in

aggregates of needles and was found to be identical with the inactive acid obtained by Fittig and Kochs (*loc. cit.*).

0.1830 (dried in a vacuum over sulphuric acid) gave 0.2695 CO<sub>2</sub> and 0.1125 H<sub>2</sub>O. C = 40.16; H = 6.8.

C<sub>4</sub>H<sub>8</sub>O<sub>4</sub> requires C = 40.0; H = 6.66 per cent.

An aqueous solution of the acid gave :

$$l = 2; c = 6.93; \alpha_D^{20} - 0.13^\circ; [\alpha]_D^{20} - 0.95^\circ.$$

On adding boric acid, in the proportion of 1 gram-molecule of the acid to 1 gram-molecule of the methylglyceric acid, the angle observed was  $-0.18^\circ$ . The specific rotation was now only  $[\alpha]_D^{20} - 1.32^\circ$ .

From these data, it is evident that the solubilities of the *d*- and *l*-brucine salts in alcohol are so nearly equal that their separation by fractional crystallisation is impossible.

*Quinine Methylglycerate.*—This salt is exceedingly soluble in water and absolute alcohol, but very sparingly so in benzene; it melts at  $174^\circ$  without decomposition. The determination of the optical activity in absolute alcohol and in water gave the following numbers respectively :

$$c = 2; l = 1; \alpha_D^{20} - 2.6^\circ; [\alpha]_D^{20} - 130^\circ.$$

$$c = 4.535; l = 1; \alpha_D^{16} - 4.94^\circ; [\alpha]_D^{16} - 108.93^\circ.$$

The specific rotation of quinine in alcohol is  $[\alpha]_D^{20} - 166.6^\circ$  ( $c = 2$ ) (Oudemann's *Annalen*, 1876, 182, 44).

The salt dissolves so sparingly in benzene and is so very soluble in water and alcohol, that it was quite impossible to separate its active components by fractional crystallisation.

The cinchonine, strychnine, and morphine salts are exceedingly soluble in water and in alcohol; the cinchonine salt is sparingly soluble in benzene. We have not as yet obtained the salts of these three bases with  $\beta$ -methylglyceric acid in a crystalline form.

*Quinidine  $\beta$ -Methylglycerate.*—This salt was prepared by neutralising a hot aqueous solution of  $\beta$ -methylglyceric acid with quinidine. On concentrating on the water-bath, the salt separated out in clusters of six-sided plates. The mother liquor gave a second crop of these crystals, but, after further concentration, needle-shaped crystals appeared. The first crop of crystals melted at  $113$ – $114^\circ$  without decomposition, and contained two molecules of water of crystallisation.

0.3 air-dried salt gave 15.6 c.c. moist nitrogen at  $16^\circ$  and 763 mm.

N = 6.08.

0.1823 air-dried salt gave 0.4015 CO<sub>2</sub> and 0.1220 H<sub>2</sub>O. C = 60.06;

H = 7.43.

0.5811 air-dried salt lost  $0.338^\circ$  at  $105^\circ$ .  $\text{H}_2\text{O} = 5.81$ .

$\text{C}_{20}\text{H}_{24}\text{O}_2\text{N}_2\text{C}_4\text{H}_8\text{O}_4, 2\text{H}_2\text{O}$  requires  $\text{N} = 5.71$ .  $\text{C} = 60.0$ ;  $\text{H} = 7.5$ ;  
 $\text{H}_2\text{O} = 7.5$ .

$\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_2\text{C}_4\text{H}_8\text{O}_4, 1\frac{1}{2}\text{H}_2\text{O}$  requires  $\text{N} = 5.82$ .  $\text{C} = 59.87$ ;  $\text{H} = 7.27$ ;  
 $\text{H}_2\text{O} = 5.73$  per cent.

The specific rotation was determined in aqueous and in alcoholic solutions.

(a) In water.  $l = 1$ ;  $c = 3.310$ ;  $\alpha_D^{16^\circ} + 4.75^\circ$ ;  $[\alpha]_D^{16^\circ} + 143.46^\circ$ .

(b) In alcohol.  $l = 1$ ;  $c = 3.7916$ ;  $\alpha_D^{16^\circ} + 4.72^\circ$ ;  $[\alpha]_D^{16^\circ} = 159.04^\circ$ .  
 $d = 0.772$ .

The specific rotation of quinidine in alcohol is  $+236.8^\circ$ .

After six crystallisations from water, neither the melting point nor optical activity underwent any appreciable change.

The sixth fraction melted at  $114^\circ$ , and had a specific rotation  $[\alpha]_D^{18^\circ} + 142.2^\circ$ .

The determination of the solubility of the salt in water gave the following numbers.

8.2738 grams of a saturated aqueous solution of quinidine  $\beta$ -methylglycerate at  $14.9^\circ$  contained 0.1368 gram of the salt; this result corresponds with a solubility at  $14.9^\circ$  of 1.64 grams in 100 grams of the solution.

### *1- $\beta$ -Methylglyceric Acid.*

The pure quinidine salt (m. p.  $114^\circ$ ) was dissolved in about 10 parts of water, and the quinidine was precipitated by means of baryta solution. The excess of baryta was removed by carbon dioxide, and, after filtration, the solution was found to be strongly laevorotatory.

The solution of the barium salt was concentrated to a small bulk *in vacuo* at  $50^\circ$  and poured into absolute alcohol. The precipitated barium salt is somewhat soluble in alcohol, and, on evaporating off this solvent, a further quantity of the salt was obtained; it was purified by recrystallisation from a very small volume of water, when it separated in fine needles and dried at  $110^\circ$ .

0.2032 gave 0.1267  $\text{BaSO}_4$ .  $\text{Ba} = 36.52$ .

$(\text{C}_4\text{H}_7\text{O}_4)_2\text{Ba}$  requires  $\text{Ba} = 36.53$  per cent.

The determination of the specific rotation gave the following numbers:

$l = 1$ ;  $c = 6.2683$ ;  $\alpha_D^{16^\circ} - 1.36^\circ$ ;  $[\alpha]_D^{16^\circ} - 20.63^\circ$ ;

and after 12 hours the rotation was unchanged.

To obtain the free acid, the barium salt was decomposed exactly by dilute sulphuric acid; the filtrate from the barium sulphate was

evaporated at  $50^\circ$  under diminished pressure to a syrup, which was extracted with dry acetone; the solution was filtered and the filtrate treated with dry ether until a permanent turbidity ensued.

The ether-acetone solution was poured off from the syrup which separated, and allowed to evaporate at the ordinary temperature. The acid, which was left as a syrup, after being stirred with a glass rod became solid. The white, crystalline solid was washed with dry ether and dried in a vacuum over sulphuric acid until its weight became constant. It was found to be quite free from ash. The *l*-methylglyceric acid crystallises in hexagonal plates and melts at  $74\text{--}75^\circ$ . Fittig and Kochs (*loc. cit.*) give the same melting point for the inactive acid.

0.1808 gave 0.2655  $\text{CO}_2$  and 0.1122  $\text{H}_2\text{O}$ .  $\text{C} = 40.05$ ;  $\text{H} = 6.89$ .

$\text{C}_4\text{H}_8\text{O}_4$  requires  $\text{C} = 40.0$ ;  $\text{H} = 6.66$  per cent.

The determination of the specific rotation gave the following numbers:

$l = 1$ ;  $c = 5.9937$ ;  $d = 1.023$ ;  $\alpha_D^{16^\circ} = 1.17^\circ$ ;  $[\alpha]_D^{16^\circ} = 13.51^\circ$ .

The acid is exceedingly hygroscopic; it is very soluble in alcohol and acetone, and dissolves very sparingly in dry ether.

#### *d*- $\beta$ -Methylglyceric Acid.

The mother liquors from the quinidine *l*-salt contain the more soluble *d*-salt. It was found impossible to separate the *l*-salt completely from the *d*-salt by fractional crystallisation. Since the barium *l*-salt is somewhat soluble in alcohol and the inactive barium salt is insoluble in that solvent, it was thought that a separation of the barium *d*-salt from the racemic salt might be effected by means of alcohol.

The impure quinidine *d*-salt was decomposed by baryta, and after filtration from the precipitated quinidine the concentrated solution of the barium salt was poured into absolute alcohol. The salt which separated out was quite inactive, and contained 36.5 per cent. of barium. The alcoholic filtrate was concentrated to a syrup, which soon became solid. After digestion with rectified spirit, the inactive salt was left undissolved, and from the alcoholic filtrate, the *d*-salt was obtained as an uncrystallisable syrup. In order to remove as much as possible of the inactive salt, the treatment with rectified spirit was repeated twice and the syrup was dried at  $130^\circ$  and analysed.

0.21479 gave 0.1350  $\text{BaSO}_4$ .  $\text{Ba} = 36.95$ .

$\text{Ba}(\text{C}_4\text{H}_7\text{O}_4)_2$  requires  $\text{Ba} = 36.53$  per cent.

A determination of the specific rotatory power gave the following numbers :

$$l = 1 ; c = 7.058 ; d = 1.040 ; \alpha_D^{15} + 1.25^\circ ; [\alpha]_D^{20} + 17.03^\circ.$$

The specific rotation of the barium *d*- $\beta$ -methylglycerate agrees fairly well with the value obtained for that of the barium *l*-salt.

The yield of the barium *d*-salt was so small, owing to the difficulty in separating it from the inactive salt, that the *d*-methylglyceric acid could not be isolated.

The racemic barium methylglycerate is much less soluble in water than either the *d*- or *l*-salt, and crystallises from a concentrated aqueous solution in stellar aggregates of obliquely terminated needles ; it contains two molecules of water of crystallisation, which are expelled at  $110^\circ$ .

0.6456 (air-dried) lost 0.0544  $\text{H}_2\text{O}$ .  $\text{H}_2\text{O} = 8.4$ .

$\text{Ba}(\text{C}_4\text{H}_7\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$  requires  $\text{H}_2\text{O} = 8.75$  per cent.

We are under very great obligations to Mr. A. E. Bellars for valuable assistance in the experimental part of the paper.

Our thanks are due to the Research Fund Committee of the Chemical Society for a grant defraying the cost of the materials used in this investigation.

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## XXVI.—*The Chemical Reactions of Nickel Carbonyl.* *Part I. Reactions with the Halogens and other* *Inorganic Substances.*

By JAMES DEWAR and HUMPHREY OWEN JONES.

THE previous investigation of the physical properties and stability of nickel carbonyl (*Proc. Roy. Soc.*, 1903, 51, 427) having shown that the compound was much more stable than had hitherto been supposed, it was thought of interest to study its chemical reactions and stability more fully.

A few of the simpler decompositions of the compound were observed by Dr. Mond and his collaborators (*Trans.*, 1890, 57, 749), some further observations were recorded by Berthelot (*Compt. rend.*, 1891, 113, 679), and the product of oxidation in moist air has been studied by the last-mentioned chemist and by Lenher and Loos (*Amer. Chem. J.*, 1899, 22, 114).

The authors have studied a number of the reactions of the compound with the view of throwing further light on its chemical nature and structure, and its possible use as a synthetical agent. The present paper contains an account of its interactions with certain elements and simple inorganic compounds, studied mainly from a thermochemical point of view.

The heat of formation of liquid nickel carbonyl from metallic nickel and gaseous carbon monoxide, as determined by Mittasch (*Zeit. Physikal. Chem.*, 1902, 40, 49), lies between 51 and 55 Cal., the mean value being 52.17 Cal. Reicher had previously obtained the value 59.5 Cal. from the combustion of the compound. Taking the lower value and Thomsen's values for other nickel compounds, it might be expected that nickel carbonyl would be readily decomposed by chlorine or bromine, but not by iodine or sulphur, whereas it is actually decomposed completely by the four elements with the production of the corresponding nickel compounds and carbon monoxide.

In no case in which nickel carbonyl has been decomposed by elements has any combination of the carbon monoxide with the element been observed. This is remarkable since it might be expected that combination would take place more readily when the monoxide was in the so-called 'nascent' state.

Again, in the decomposition with hydrogen iodide and hydrogen sulphide, carbon monoxide is set free, and combination with hydrogen does not occur to any appreciable extent, if at all.

### *The Halogens and their Compounds.*

The reaction with the halogens was investigated in solution in pure, dry carbon tetrachloride, the mode of procedure being briefly as follows. Standard solutions of the carbonyl derivative and the halogen were made, varying in strength from normal to decinormal, 1—10 c.c. of the carbonyl solution were introduced into a Lunge nitrometer over mercury followed successively by some tetrachloride and a very slight excess of the solution of the halogen, the mixture being then shaken and the volume of gas evolved measured after the reaction was completed. This volume was then corrected to normal temperature and pressure by comparison with another nitrometer containing a known volume of air enclosed over carbon tetrachloride, and the gas was afterwards examined to ascertain whether it was pure carbon monoxide.

Experiments were also made at low temperatures to see whether the liquid or solid halogens had any action on solid nickel carbonyl.

*Chlorine.*

On mixing normal solutions in carbon tetrachloride, a brisk evolution of gas takes place at once and a grey solid is precipitated. From 1 c.c. of normal nickel carbonyl solution and 1.1 c.c. of normal chlorine solution, 49.0 c.c. of gas at 16° and 755 mm. were evolved, the volume when corrected to 0° and 760 mm. being 45.2 c.c.

The volume of carbon monoxide theoretically obtainable being 44.8 c.c., it is clear that complete decomposition has taken place into carbon monoxide or a mixture of this gas and carbonyl chloride. The gas, when tested for carbonyl chloride by treatment with water or aqueous sodium carbonate, gave indications that at most only a trace of the gas was formed, even when a considerable excess of chlorine had been used.

The solid product when collected and analysed was found to be pure anhydrous nickel chloride.

The heat of the reaction  $[\text{Ni}, \text{Cl}_2]$  is given by Thomsen (*Thermochemische Untersuchungen*, 3, 307) as 74.53 Cal., hence the reaction  $[\text{Ni}(\text{CO})_4, \text{Cl}_2]$  should occur with the evolution of 22.36 Cal.: a considerable rise of temperature does occur during the reaction.

No action occurs in a mixture of solid chlorine and solid nickel carbonyl, but when the chlorine becomes liquid the reaction seems to begin and to proceed steadily.

*Bromine.*

The reaction between normal solutions in carbon tetrachloride takes place rapidly and ends almost immediately after complete mixture, as in the case of chlorine.

The gas evolved was pure carbon monoxide and the solid on analysis was found to be pure anhydrous nickel bromide.

One c.c. of nickel carbonyl solution and 1.1 c.c. of normal bromine solution gave 47.2 c.c. of gas at 12° and 758 mm. The corrected volume of the gas is 44.5, whereas theory requires 44.8 as before.

Thomsen (*loc. cit.*) gives the heat of the reaction  $(\text{Ni}, \text{Br}_2, \text{aq})$  as 71.82 Cal., so that, unless the heat of hydration of nickel bromide is exceptionally great and the heat of solution exceptionally small, the reaction  $[\text{Ni}(\text{CO})_4, \text{Br}_2]$  should nevertheless occur with evolution of heat, as is actually found to be the case: a distinct rise of temperature takes place during the reaction.

Solid nickel carbonyl and solid bromine did not react, and when the mixture was gradually warmed it underwent no change until the bromine became liquid, when the reaction between the solid carbonyl and the liquid bromine proceeded rapidly.

*Iodine.*

When a normal solution of nickel carbonyl in carbon tetrachloride was mixed with an  $N/5$  or  $N/10$  solution of iodine in the same solvent, a brown or black solid was deposited and carbon monoxide was slowly evolved. On examination the solid proved to be nickel iodide. The reaction between 1 c.c. of the carbonyl solution and 5 c.c. of  $N/5$  iodine solution was completed in about half an hour, and the theoretical quantity of carbon monoxide was produced, as in the other cases.

Analysis of the solid, after heating at  $100^\circ$ , gave  $\text{Ni}=18.9$ .  $\text{I}=80.6$ . Calculated for  $\text{NiI}_2$ ,  $\text{Ni}=18.9$ .  $\text{I}=81.1$  per cent.

Thomsen (*loc. cit.*) gives the heat of the reaction  $(\text{NiI}_2, \text{aq})$  as 41.4 Cal. Now, unless the sum of the heats of hydration and solution of nickel iodide is negative, the reaction  $[\text{Ni}(\text{CO})_4, \text{I}_2]$  should be endothermic. A rough experiment was made which showed that the combined heat of solution and hydration of nickel iodide was positive, but small, being approximately 614 cal.

It was therefore important to determine whether any considerable fall of temperature occurred during the reaction. Experiments were made in which a definite volume of normal nickel carbonyl solution in different solvents was placed in a bulb, which was broken in an excess of  $N/10$  iodine dissolved in the same solvent and contained in a bottle, insulated as far as possible from extraneous sources of heat. The mixture was stirred, and the change of temperature observed by means of an accurate thermometer.

A mixture of 80 c.c. of  $N/5$  iodine and 8 c.c. of normal nickel carbonyl in carbon tetrachloride, was initially at  $15^\circ$ , and in the course of 13 minutes the temperature fell to  $13.8^\circ$ , the reaction being by that time nearly completed.

A mixture of 80 c.c. of  $N/10$  iodine, and 7 c.c. of normal nickel carbonyl in alcohol, was initially at  $15.4^\circ$ , but after 23 minutes, when the reaction was practically completed, the temperature had fallen to  $14.7^\circ$ .

In both these cases the fall is scarcely greater than would be expected to occur by the evaporation of a quantity of the liquid necessary to saturate the carbon monoxide evolved with its vapour at the temperature of the experiment. Sufficient data are not available to calculate the expected fall of temperature accurately, but the rough estimate which can be made with the incomplete data obtainable is of the above order.

It became, therefore, interesting to ascertain the source of the energy necessary to carry out the reaction. Experiments described

below on the velocity of the evolution of the carbon monoxide show that the reaction proceeds steadily at the ordinary temperature, and is a normal bimolecular reaction, as might be expected. The energy cannot be derived from radiant light or heat, since the reaction proceeds quite as rapidly when such radiations are screened off as completely as possible.

An indication of the possible source of the energy was obtained when the reaction was carried out in ethereal solution. In this case the nickel iodide is usually first deposited as a viscid brown liquid, which then changes into a mass of large pale green, tabular crystals, but very occasionally the green crystals seem to be formed directly. These crystals, when filtered off rapidly, change to the black iodide, and give off ether in the process; they may therefore be considered as consisting of nickel iodide united with ether of crystallisation.\* The loss of ether is so rapid when the crystals are taken out of the solvent, that it is quite impossible to analyse them. Somewhat similar phenomena have also been observed in other solvents, for example, in chloroform the iodide is deposited in brown, tabular crystals, which rapidly change when removed from the solution, and it is therefore probable that the nickel iodide forms molecular complexes either with the solvent or with iodine, even when there is no visible evidence of their existence, and thus gains the energy necessary to carry out the reaction. However, the tendency to form these complexes cannot be very great, since the anhydrous iodide does not combine with these solvents when mixed with them at the ordinary temperature.

This hypothesis as to the source of the energy required receives some slight support from the fact that solid iodine has scarcely any action on liquid nickel carbonyl, although this is partly due to the fact that the halogen is insoluble in the latter.

### *The Order of the Reaction and its Velocity in Chloroform.*

On investigating the velocity of the reaction in chloroform solution by observing the rate of evolution of carbon monoxide, it was found that the reaction proceeded quite normally at the ordinary temperature and, by altering the concentration, it was found that the reaction was of the second order as might be expected from the equation  $\text{Ni}(\text{CO})_4 + \text{I}_2 = \text{NiI}_2 + 4\text{CO}$ , providing that the iodine molecules are diatomic in chloroform solution. The experiments were made as simple as possible, the object being merely to see that the reaction proceeded steadily.

Three experiments are quoted and the results are shown by the appended curves, in which the ordinates represent the number of cubic

\* Compare the formation of  $\text{MgBr}_2 \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$  and  $\text{MgI}_2 \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$  (*Compt. rend.*, 1901, 132, 835) and (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 610).

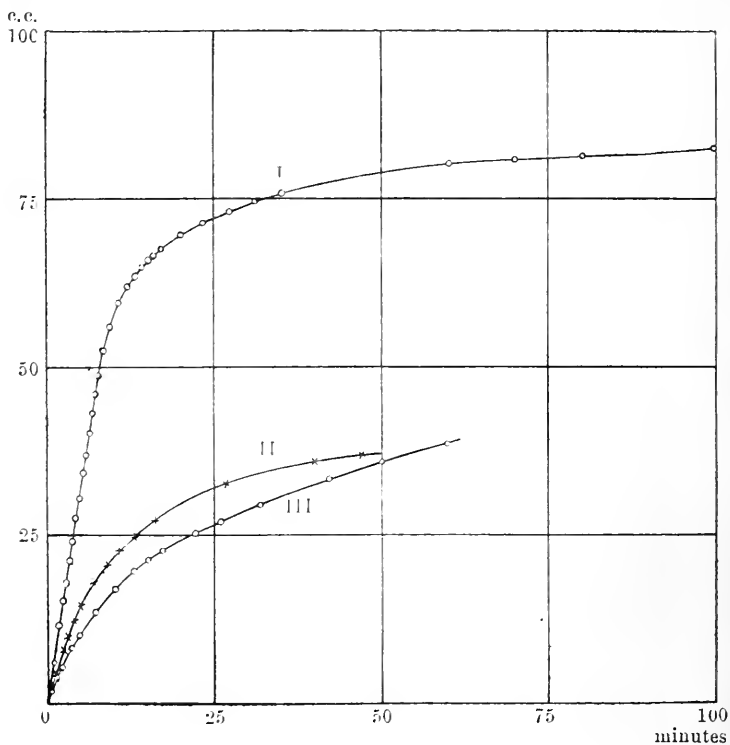
centimetres of gas evolved and the abscissæ represent the time in minutes, the temperature being  $12^{\circ}$ .

Curve I, 10 c.c.  $N/5$   $Ni(CO)_4$  + 30 c.c.  $N/10$  iodine in 50 c.c.

„ II, 5 „  $N/5$   $Ni(CO)_4$  + 30 „  $N/10$  iodine in 50 „

„ III, 5 „  $N/5$   $Ni(CO)_4$  + 15 „  $N/10$  iodine in 50 „

It is readily seen that the evolution of gas proceeds steadily without cessation from the beginning to the time when the observations ceased.



The order of the reaction was calculated by means of the formula

$$n = \frac{\log dC_1/dt / dC_2/dt}{\log C_1/C_2}$$

for three pairs of experiments I and III, and the following three values of  $n$  were obtained, 2.03, 2.20, and 2.00, so that the reaction is evidently one of the second order.

In calculating the velocity constant, very satisfactory results cannot

be obtained, probably owing either to some lag in the evolution of the gas from the solvent or to some disturbing side reactions. The value of  $k$ , however, appears to be about 0.0005, the unit of time being a minute.

### *Cyanogen.*

Gaseous cyanogen appears to have no action on gaseous or liquid nickel carbonyl. Cyanogen gas, enclosed in a Lunge nitrometer over mercury, when mixed with a little nickel carbonyl immediately increased in volume owing to the high vapour pressure of the carbonyl; but afterwards the volume remained constant for several days and no solid was deposited.

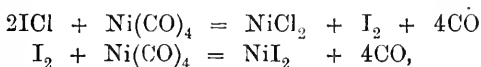
With an alcoholic solution of cyanogen, however, a reaction took place with moderate ease, nickel cyanide and carbon monoxide being produced. The reaction proceeded to the end, and the theoretical quantity of gas was evolved.

The heat of formation of hydrated nickel cyanide is 50.5 Cal. (Varet, *Compt. rend.*, 1896, 122, 1123), it is therefore slightly greater than that of nickel iodide, so that the reaction here, again, must be promoted by the formation of molecular complexes as in the case of the iodide.

### *Iodine Monochloride.*

When the brown solution of iodine monochloride in chloroform is mixed with a solution of nickel carbonyl in the same solvent, a violent reaction immediately takes place, a light brown solid is precipitated, and the solution becomes purple. The rate of evolution of gas then diminishes appreciably and the purple colour of the solution gradually disappears. The gas evolved is carbon monoxide, and the solid product of the reaction is a mixture of nickel chloride and iodide.

The reaction obviously proceeds in two distinct stages according to the equations



the first stage taking place rapidly with liberation of iodine, which then reacts more slowly with a further quantity of nickel carbonyl.

### *Iodine Trichloride.*

The reaction here proceeds exactly as in the case of the monochloride. The brown solution in chloroform or carbon tetrachloride at once becomes purple and gas is evolved very rapidly; the evolution of gas then becomes slower and the purple colour gradually disappears. The

reaction clearly occurs in two distinct stages, as in the case of the monochloride, the chloride being formed in preference to the iodide as would be expected from their respective heats of formation.

### *Cyanogen Iodide.*

When the colourless alcoholic solution of cyanogen iodide is mixed with a similar solution of nickel carbonyl, a light drab precipitate is at once formed, carbon monoxide is evolved and the solution turns brown. The precipitate is nickel cyanide and free iodine remains in the solution. The evolution of gas continues, and a darker precipitate is produced which now consists of nickel iodide.

A chloroform solution of cyanogen iodide, which is also colourless, behaves similarly, gas is evolved and a light drab precipitate produced, the solution becoming purple and containing free iodine. The evolution of gas continues and the precipitate turns black, or, if the tube is not shaken, a black precipitate of nickel iodide settles on the top of that first formed.

Here, again, it is clear that the reaction proceeds in stages, nickel cyanide and free iodine being first formed according to the equation



and then the iodine reacts with a further quantity of nickel carbonyl to produce nickel iodide. This shows clearly that the heat of formation of nickel cyanide is greater than that of the iodide in alcoholic or chloroform solutions, just as in aqueous solution.

### *The Hydrides of the Halogens.*

Dry hydrogen chloride or bromide, when mixed with nickel carbonyl over mercury, at once increases in volume owing to the vapour pressure of the carbonyl, the increase being exactly that amount which would be expected from the known value of the vapour pressure. Practically no further change could be observed on allowing the mixture to remain for several days. A minute amount of solid was deposited in some cases, but there was obviously no extensive reaction.

The reaction between hydrogen iodide and nickel carbonyl was investigated as follows, the use of mercury being inadmissible on account of its action on the acid gas. A glass bulb was carefully exhausted and then filled with hydrogen iodide at a slightly reduced pressure, a little nickel carbonyl was then admitted, excess being avoided at first. The gases soon reacted with the deposition of a black solid, the gaseous products were examined by passing through a U-tube immersed in liquid air and collecting the uncondensable gas and afterwards fractionating the condensed portions. The uncondensed gases

consisted of hydrogen and carbon monoxide, the condensable part being hydrogen iodide and nickel carbonyl. No formaldehyde could be detected. The solid produced was pure nickel iodide and contained no free iodine.

A solution of hydrogen iodide in chloroform reacts very rapidly with a similar solution of nickel carbonyl, producing carbon monoxide and a mixture of solids containing nickel iodide and free iodine, which has not yet been fully examined.

### *Sulphur.*

A solution of sulphur in carbon disulphide reacts slowly with nickel carbonyl in the absence of air, evolving a gas and forming a black solid. The gas evolved is not immediately absorbed by an alcoholic potash solution and therefore contains no carbon oxysulphide, it is, however, taken up by a solution of cuprous chloride in hydrochloric acid and is therefore practically pure carbon monoxide. The solid contains nickel and sulphur. A similar reaction occurs with a solution of sulphur in xylene, but in both cases it takes place very slowly.

With 1.5 c.c. of a normal solution of nickel carbonyl and an excess of a solution of sulphur in carbon disulphide, gas was steadily evolved for four days until about 78 c.c. had been collected, this being approximately the amount to be expected.

The heat of the reaction ( $\text{Ni}_3\text{S}_2.n\text{H}_2\text{O}$ ) is given by Thomsen (*loc. cit.*) as 19.4 Cal., so that the reaction  $[\text{Ni}(\text{CO})_4]\text{S}$  might therefore be strongly endothermic. However, there is no marked fall of temperature during the reaction, no energy can be obtained from radiant light since the black deposit rapidly renders the walls of the vessel quite opaque, and moreover, the reaction proceeds in the dark. The solid, on examination, was found to be a higher sulphide than  $\text{NiS}$ , having, in fact, a composition closely corresponding to  $\text{Ni}_2\text{S}_3$ . Found  $\text{Ni} = 54.8$ .  $\text{Ni}_2\text{S}_3$  requires  $\text{Ni} = 54.5$  per cent. Hence the necessary energy may be derived from the formation of this more complex compound.

### *Hydrogen Sulphide.*

Hydrogen sulphide mixed with excess of nickel carbonyl reacts very slowly, depositing a black solid and liberating hydrogen and carbon monoxide. In about a week only about 40 per cent. of the sulphide had reacted.

In alcoholic solution, the reaction proceeds more quickly, and the black precipitate first formed acquires a bronze lustre. On analysis, this solid proved to be the monosulphide,  $\text{NiS}$ . Found  $\text{Ni} = 64.4$ .  $\text{NiS}$  requires  $\text{Ni} = 64.7$  per cent.

The gases evolved contained hydrogen and carbon monoxide, and no formaldehyde could be identified with certainty among the products of reaction.

*Sulphuric Acid.*

Berthelot (*Compt. rend.*, 1891, 112, 1343) states that nickel carbonyl in contact with concentrated sulphuric acid detonates after a few minutes. This is quite contrary to our experience, for even when slightly moist nickel carbonyl was used, the reaction always took place slowly without any great evolution of heat.

Some nickel carbonyl and sulphuric acid were sealed up in a tube, a reaction went on very slowly during several weeks. The tube was opened from time to time and examined. Considerable pressure was developed and a yellow precipitate was formed. The gas evolved was a mixture of carbon monoxide and hydrogen, a little hydrogen sulphide was observed later, and the yellow solid proved to be nickel sulphate, so that the reaction seems to proceed according to the equation:



*Phosphorus.*

Nickel carbonyl, when mixed with a solution of phosphorus in carbon disulphide and left out of contact with air, undergoes no change after several weeks. If, however, dry air has access to the mixture, a reaction slowly occurs with the evolution of gas and the formation of a black solid which contains nickel and phosphorus, but which has not yet been fully examined.

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XXVII.—*The Chemical Reactions of Nickel Carbonyl.*  
*Part II. Reaction with Aromatic Hydrocarbons*  
*in presence of Aluminium Chloride. Synthesis of*  
*Aldehydes and Anthracene Derivatives.*

By JAMES DEWAR and HUMPHREY OWEN JONES.

NICKEL carbonyl does not react with aluminium chloride or most of the other metallic chlorides, nor has it by itself any action on aromatic hydrocarbons. If, however, a mixture of nickel carbonyl and a hydrocarbon, such as benzene or toluene, is treated with aluminium chloride

in the cold, a rapid evolution of hydrogen chloride at once occurs, while the mixture darkens in colour and becomes viscid. It is remarkable that during this apparently violent reaction there is no perceptible rise of temperature.

The reaction was allowed to proceed in the cold and also at  $100^{\circ}$ , and the products investigated. In the former case, an aldehyde was produced, the reaction being very similar to that effected by a mixture of carbon monoxide and hydrogen chloride in the presence of aluminium chloride (Gattermann and Koch, *Ber.*, 1897, 30, 1622; 1898, 31, 1149), and little or no nickel chloride could be detected. In the latter case, the aldehyde had almost entirely disappeared; an anthracene derivative was found to have been produced whenever possible, and a considerable quantity of nickel chloride appeared among the reaction products. The mechanism of this reaction is obscure, and although it is probable that the anthracene is formed by the condensation of two molecules of the aldehyde with the elimination of the elements of hydrogen peroxide, a change which may be effected by the metallic nickel present, yet numerous experiments made with the view of throwing further light on the process have given negative results.

The aldehyde produced from toluene is *p*-tolualdehyde, and the dimethylantracene formed must then be 2:6-dimethylantracene.

*m*-Xylene gives 2:4-dimethylbenzaldehyde, and the tetramethylantracene is therefore the 2:4:6:8-derivative, since the aldehyde can only condense in one way so as to give an anthracene compound. This tetramethylantracene is identical with that produced by Anschütz from *m*-xylene. Consequently the other produced from *m*-xylene by Friedel and Crafts must be the 1:3:6:8-isomeride, since there are only two such compounds which can be derived from *m*-xylene.

Mesitylene gives the aldehyde and no condensation product, the formation of an anthracene derivative being impossible in this case.

Naphthalene behaves in an entirely different manner from the above benzene derivatives; no aldehyde could be detected, and the product contains a hydrocarbon,  $C_{16}H_{12}$ , apparently identical with that obtained from ruficoccin by distillation with zinc dust and also by the action of methyl chloride and aluminium chloride on naphthalene. In this case, it would appear that carbon rings have been formed directly from carbon monoxide.

#### *Benzene.*

A mixture of benzene (4 mols.), aluminium chloride (4 mols.), and nickel carbonyl (1 mol.) was allowed to react in the cold either in a flask provided with a calcium chloride tube with a very small orifice as outlet for the gas, or in a sealed tube, which was opened from time to time to relieve the pressure. After a few days, the dark mass was

decomposed by means of ice-water (the aqueous layer contained only mere traces of nickel in solution), and after the addition of hydrochloric acid was submitted to distillation in a current of steam. The distillate and residue were extracted with benzene, dried over calcium chloride, and distilled. The distillate in steam was found to consist almost entirely of benzaldehyde, which was further identified by oxidation to benzoic acid and by the formation of its phenylhydrazone. The yield obtainable is not large, not exceeding 25 per cent. of the weight of the benzene used. The residue not volatile in steam was found to contain only a small quantity of viscid oil, which was not further examined.

On heating a mixture of the reagents, in the same proportions as above, at  $100^{\circ}$  in a sealed tube for periods varying from half an hour to several hours, the result was invariably the same, a dark mass was formed, considerable pressure developed, and a certain amount of the three reagents was found to be still present.

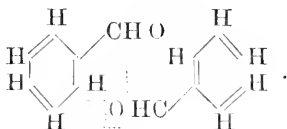
The product of the reaction was mixed with ice-water and treated as already described; the aqueous layer now contained considerable quantities of nickel in solution. The distillate in steam yielded a small quantity of benzaldehyde and a trace of a crystalline solid, which was afterwards found to be identical with the substance isolated from the part not volatile in steam. The dark, tarry solid left in the flask after the distillation in steam was taken up in hot benzene and the solution dried over calcium chloride and distilled under reduced pressure. A crystalline solid having a pale yellow colour distilled over between  $250^{\circ}$  and  $260^{\circ}$  under 10 mm. pressure, leaving behind a small amount of tarry residue, which was not further investigated. In one experiment, 12 grams of the solid were obtained, together with a small amount of benzaldehyde, from 17 grams of nickel carbonyl and 31.2 grams of benzene.

The solid, which was repeatedly crystallised from hot alcohol or benzene, was finally obtained in colourless, lustrous plates melting at  $211^{\circ}$  (uncorr.), and showing a beautiful violet fluorescence; it was identified as anthracene by ultimate analysis and vapour density determinations, and was further characterised by the formation of its picrate (m. p.  $136-137^{\circ}$ ) and anthraquinone.

Moreover, it was found that both this product and pure anthracene dissolved in pure sulphuric acid to a pale yellow solution, but if a trace of nitric acid were present—as is always the case with the ordinary 'pure' acid—a brilliant, dark green coloration was produced, and on adding potassium dichromate or a larger amount of nitric acid, the colour changed to a brilliant, reddish-purple, and finally to brown. This reaction, which we have never seen described, constitutes an ex-

ceedingly delicate test for anthracene and its homologues, and serves to distinguish this series from allied substances.

Anthracene is therefore the principal product of the action of nickel carbonyl on benzene in the presence of aluminium chloride at  $100^{\circ}$ , and it seems that benzaldehyde is certainly an intermediate product. The mechanism of this reaction, if benzaldehyde is assumed to be the intermediate product, consists in the elimination of the elements of hydrogen peroxide.



This change is of considerable interest, and several experiments have been made with the object of elucidating it; but, unfortunately, little information has been gained. The metallic nickel, produced by the decomposition of its carbonyl derivative, is very probably the reducing agent which effects the change, since it is only dissolved in any quantity when anthracene is produced.

(1) Benzaldehyde, when heated with aluminium chloride alone or with benzene and aluminium chloride, produced no anthracene, but only benzoic acid and a solid melting at  $90^{\circ}$ .

(2) On heating with aluminium chloride and zinc dust, benzaldehyde yielded a solid not volatile in steam; this product dissolved in hot alcohol and crystallised in needles melting at  $134^{\circ}$ .

0.1223 gave 0.356  $\text{CO}_2$  and 0.0625  $\text{H}_2\text{O}$ .  $\text{C} = 78.8$ ;  $\text{H} = 5.6$ .

$(\text{C}_6\text{H}_5 \cdot \text{CHO})_x$  requires  $\text{C} = 79.2$ ;  $\text{H} = 5.6$  per cent.

The substance is identified as being benzoin by the foregoing analysis and by a comparison of its melting point with that of the pure substance.

(3) A mixture of benzaldehyde, aluminium chloride, and finely-divided metallic nickel (reduced at a low temperature), when left in the cold became hot, and a small quantity of gas was produced. The product was heated at  $100^{\circ}$  for 5 hours and then examined in the manner already described. There was a slight pressure in the tube, and the aqueous solution contained nickel chloride. The steam distillate contained benzaldehyde and benzoic acid, but no anthracene could be obtained.

Hydrogen chloride, in benzene solution, was found to have only a very slight action on nickel carbonyl. Zinc chloride and anhydrous ferric chloride cause the production of a small amount of hydrogen

chloride, but the action is very slight and the liquid remains clear and colourless even after prolonged heating.

### *Toluene.*

On mixing nickel carbonyl (1 mol.) with toluene (4 mols.) and aluminium chloride (4 mols.), torrents of hydrochloric acid were immediately evolved, and the evolution of gas from the mixture continued slowly for several days. The reaction product was treated successively with ice-water and hydrochloric acid, being then submitted to steam distillation and worked up as already described. The aqueous solution contained only a trace of nickel chloride. Toluene distilled over first, and then a small quantity of oil boiling at  $204^{\circ}$  was obtained, the yield being about 16 per cent. of the toluene used. This product was identified as *p*-tolualdehyde by the preparation of methyl terephthalate from the product of its oxidation. The phenylhydrazone of this aldehyde was prepared; it separated from alcoholic solution in almost colourless plates which melt at  $114$ – $115^{\circ}$  and readily turn pink on exposure to sunlight. There was a small amount of non-crystallisable oil with a high boiling point, which was not further examined.

The product of the reaction at  $100^{\circ}$ , worked up in a similar way, gave about 9 per cent. of the aldehyde, and then the residue gave a solid, which, on crystallising from hot alcohol, separated in plates melting at  $215$ – $216^{\circ}$ .

0.1566 gave 0.5330  $\text{CO}_2$  and 0.099  $\text{H}_2\text{O}$ .  $\text{C} = 92.9$  ;  $\text{H} = 7.02$ .

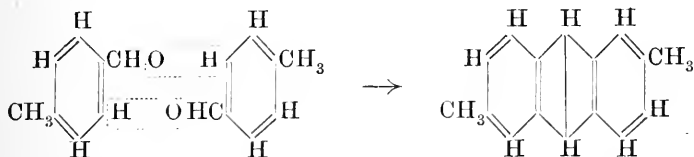
$\text{C}_{10}\text{H}_{14}$  requires  $\text{C} = 93.2$  ;  $\text{H} = 6.8$  per cent.

The substance is therefore a *dimethylantracene*.

This hydrocarbon gives the same colour reactions as anthracene with sulphuric and nitric acids, the colour being a little more intense. On oxidation with an acetic acid solution of chromic acid, it gave a quinone which melted at  $159$ – $160^{\circ}$ .

Elbs and Wittich (*Ber.*, 1885, 18, 348), by the action of chloroform and aluminium chloride on toluene in carbon disulphide solution, obtained a dimethylantracene melting at  $215$ – $216^{\circ}$ , and producing a quinone melting at  $161$ – $162^{\circ}$ . This hydrocarbon is probably identical with that described above. A similar hydrocarbon melting at  $231$ – $232^{\circ}$ , usually assumed to be identical with that of Elbs and Wittich, has been prepared by Friedel and Crafts (*Ann. Chim. Phys.*, 1884, [vi], 1, 482) by the action of benzyl chloride and aluminium chloride on toluene, and also by the action of methylene chloride and aluminium chloride on toluene (*loc. cit.*, 11, 266). The constitution of the dimethylantracene prepared by these methods has not been determined.

If, as is probable, *p*-tolualdehyde is an intermediate product in the formation of the anthracene derivative, then the constitution of the dimethylantracene thus produced, and consequently that of Elbs and Wittich, is at once fixed, since *p*-tolualdehyde can only condense in one way giving 2 : 6-dimethylantracene,



This dimethylantracene is therefore probably not the same as that obtained by Louise (*Ann. Chim. Phys.*, 1885, [vi], 6, 18); this substance, which melted at 218–219° and yielded a quinone melting at 170°, was prepared by passing benzylmesitylene through a red hot tube. These two hydrocarbons could not, however, be identical unless some profound molecular rearrangement had taken place.

#### *m*-Xylene.

A mixture of *m*-xylene, nickel carbonyl, and aluminium chloride in the proportions employed in the preceding examples at once darkened and a rapid evolution of hydrogen chloride occurred. The reaction product was allowed to remain for several days and then worked up in the manner already described. The distillate in steam gave an approximately 20 per cent. yield of an aldehyde boiling at 215–220°, and a very small quantity of an oil with a high boiling point; there was a small amount of tarry residue left in the distillation flask.

The aldehyde, on oxidation with chromic or nitric acids or when left exposed to the air, gave an acid which, after recrystallisation from hot water, was obtained as long, lustrous prisms melting at 126°.

0.1355 gave 0.3560 CO<sub>2</sub> and 0.0838 H<sub>2</sub>O. C = 71.66; H = 6.87.

C<sub>6</sub>H<sub>3</sub>(CH<sub>3</sub>)<sub>2</sub>·CO<sub>2</sub>H requires C = 72.0; H = 6.7 per cent.

The acid is therefore 2 : 4-dimethylbenzoic acid (xylic acid), identical with that produced by the action of carbonyl chloride and aluminium chloride on *m*-xylene (Ador and Meier, *Ber.*, 1879, 12, 1968). Accordingly the aldehyde is 2 : 4-dimethylbenzaldehyde, identical with that produced by the action of carbon monoxide, hydrogen chloride, and aluminium chloride on *m*-xylene by Gattermann and Koch (*loc. cit.*). The phenylhydrazone of this aldehyde crystallises from alcohol in pale yellow, rhombic plates melting at 82–84°. It has a great tendency to separate as an oil, and decomposes rapidly in sunlight, becoming coloured and gummy.

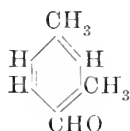
The mixture was also heated at  $100^{\circ}$  for several hours in a sealed tube and the products worked up as before. The part which volatilised in steam gave an approximately 20 per cent. yield of the aldehyde, just as if the reaction had proceeded in the cold. The residue in the distilling flask yielded a quantity of a solid boiling above  $280^{\circ}$  under 20 mm. pressure and a non-crystallisable oil with a higher boiling point. The solid was crystallised successively from hot benzene and from hot acetic acid, and was obtained in beautiful, lustrous plates melting at  $280^{\circ}$  and having a slight yellow tinge with a brilliant green fluorescence. This hydrocarbon is sparingly soluble in cold ether, alcohol, benzene and acetic acid, but more soluble in the hot solvents; it is fairly soluble in cold chloroform.

0.2698 gave 0.9097  $\text{CO}_2$  and 0.1875  $\text{H}_2\text{O}$ .  $\text{C} = 91.9$ ;  $\text{H} = 7.72$ .

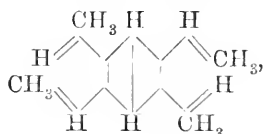
$\text{C}_{18}\text{H}_{18}$  requires  $\text{C} = 92.3$ ;  $\text{H} = 7.7$  per cent.

The compound gives a yellowish-brown coloration when dissolved in sulphuric acid with a trace of nitric acid; the solution, on further addition of the latter acid, assumes a claret, or an intense reddish-purple colour. On oxidation with chromic acid dissolved in acetic acid, a quinone was obtained, which, on recrystallisation from hot alcohol or acetic acid, formed pale yellow prisms melting at  $228$ — $230^{\circ}$ .

The hydrocarbon is therefore a *tetramethylanthracene*, and appears to be identical with that prepared by Anschütz (*Annalen*, 1886, 235, 174) by the action of acetylene tetrabromide and aluminium chloride on *m*-xylene. Since the aldehyde



can only condense in one way, the compound produced must be 2:4:6:8-tetramethylanthracene having this constitution:



unless, during the reaction, a considerable transformation has taken place resulting in the change of position of the methyl groups.

The quinone described above is therefore 2:4:6:8-tetramethylanthraquinone.

Friedel and Crafts (*Ann. Chim. Phys.*, 1887, [vi], 11, 268) obtained a tetramethylanthracene by the action of methylene chloride and

aluminium chloride on *m*-xylene, which is certainly different from that obtained by the authors and by Anschütz, since it melts at 162—163° and gives a quinone melting at 235°. This hydrocarbon must be 1 : 3 : 6 : 8-tetramethylanthracene, since this is the only other possible derivative obtainable from *m*-xylene.

### *Mesitylene.*

Mixtures of mesitylene (4 mols.), aluminium chloride (4 mols.), and nickel carbonyl (1 mol.) were either allowed to remain in the cold or heated in sealed tubes for several hours at 100°. The result in both cases was the same. On opening the tubes, there was but little pressure due to hydrogen chloride as compared to that observed with benzene and toluene, and on treating with water only a comparatively small quantity of nickel went into solution. After acidification, the liquid was submitted to distillation in steam, when the whole of the oil passed over leaving only a very small quantity of tarry matter in the distilling flask. The distillate was extracted with ether, dried over calcium chloride, and submitted to fractional distillation. The main portion of the liquid was found to be unchanged mesitylene, the remainder was an oil boiling at 234—240° and having the characteristics of an aldehyde. This oil, when oxidised with the calculated quantity of potassium permanganate in an alkaline solution, yielded an acid which was sparingly soluble in cold water and, on crystallisation from hot water, melted at 152°.

0.1072 gave 0.2865 CO<sub>2</sub> and 0.0725 H<sub>2</sub>O. C = 72.89 ; H = 7.51.

C<sub>6</sub>H<sub>2</sub>(CH<sub>3</sub>)<sub>3</sub>·CO<sub>2</sub>H requires C = 73.17 ; H = 7.32 per cent.

The substance is therefore mesitylenecarboxylic acid (m. p. 152°), the aldehyde being 2 : 4 : 6-trimethylbenzaldehyde, the boiling point of which is given as 235—240° by Feith (*Ber.*, 1891, 24, 3544); this compound cannot condense to form an anthracene derivative.

In the present instance, the reaction is very incomplete, thus, after heating at 100° for 6 hours, only 2 grams of the aldehyde were obtained from 24 grams of mesitylene. In a similar experiment, in which the heating lasted 16 hours, only a small quantity of aldehyde was obtained, but a little mesitylenecarboxylic acid was also produced (compare the formation of benzoic acid, page 215).

### *Naphthalene.*

Mixtures of naphthalene, nickel carbonyl, and aluminium chloride in the proportions indicated in the preceding experiments, when allowed to remain in the cold, gradually became very dark and slowly

evolved hydrogen chloride. After about a week, the mass was worked up in the manner already described. The distillate in steam which solidified was found to be practically pure naphthalene, and no product of an aldehydic nature was found. The black solid left in the distilling flask was dissolved in benzene, dried over calcium chloride, and, after evaporating off the benzene, was distilled under diminished pressure. At first a small amount of naphthalene distilled over, at about  $280^{\circ}$  under 17 mm. pressure an oil distilled which afterwards solidified, then above  $300^{\circ}$  the oily fraction, which had an orange colour, only partially solidified, and a small amount of black residue was left in the distilling flask.

When the same mixture had been heated at  $100^{\circ}$  for a few hours in a sealed tube and worked up as before, the same products were obtained, but in different proportions. There was now only a small quantity of naphthalene, together with a certain amount of the solid distillate and more of the oily fraction, but the main product remained in the distilling flask as a hard, black, resinous residue decomposing at the temperature at which the glass began to soften. The two last-mentioned substances still await further investigation.

The principal solid product obtained when the reaction was carried out in the cold or when the heating only continued for a very short time, was purified by repeated crystallisation from hot benzene, and was then isolated in lustrous plates having a yellow tinge and melting at  $180-181^{\circ}$ . This substance is very sparingly soluble in cold alcohol, benzene and acetic acid, much more so in the hot solvents, and especially in benzene or ethylene dibromide; its solutions are fluorescent. The colour of the hydrocarbon was diminished by crystallisation from hot alcohol with the addition of animal charcoal, but the melting point remained unchanged. From its solution in ethylene dibromide, the compound was obtained in colourless plates melting at  $180-181^{\circ}$ , the fluorescence of which still persists.

0.1203 gave 0.4100  $\text{CO}_2$  and 0.0610  $\text{H}_2\text{O}$ .  $\text{C} = 93.7$ ;  $\text{H} = 5.63$ .

0.1371 „ 0.4722  $\text{CO}_2$  „ 0.0711  $\text{H}_2\text{O}$ .  $\text{C} = 93.9$ ;  $\text{H} = 5.76$ .

$(\text{C}_5\text{H}_4)_x$  requires  $\text{C} = 93.75$ ;  $\text{H} = 6.25$ .

$(\text{C}_4\text{H}_3)_x$  „  $\text{C} = 94.11$ ;  $\text{H} = 5.89$ .

$(\text{C}_4\text{H}_4)_x$  „  $\text{C} = 92.7$ ;  $\text{H} = 7.3$  per cent.

A determination of the vapour density was made by V. Meyer's method, using a lead bath heated to a high temperature.

0.0712 gave 8.4 c.c. at  $12^{\circ}$  and 774 mm.  $\text{M. W.} = 196.4$ .

After cooling the apparatus, it was found that the hydrocarbon had sublimed in lustrous plates without charring.

Several determinations of the molecular weight were made by the

cryoscopic method with carefully purified ethylene dibromide as solvent. Test experiments with naphthalene and anthracene served to show that the solvent was pure and gave very satisfactory numbers. The experimental errors in the determination of the depression are necessarily large, since with solutions nearly saturated, as, for example, with 0.11 gram of the substance in 41 grams of solvent, the depression was only  $0.16^\circ$ , so that accurate results could not be expected. The following values were obtained: M. W. = 193. 198. 214. 227.

Attempts were made to use acetic acid or benzene for the cryoscopic method, but the hydrocarbon was too sparingly soluble in these solvents. With phenol, the value 215 was obtained, but the depression observed with a nearly saturated solution was only  $0.08^\circ$ . By the ebullioscopic method with alcohol as solvent, the elevation was too small to give reliable results, but in benzene the values 263 and 234 were obtained.

Mr. G. Barger, B.A., of King's College, kindly determined the molecular weight of the hydrocarbon by means of his microscopic method (this vol, p. 286). The sparing solubility again makes the determinations difficult, and largely increases the experimental error.

A solution in benzene containing 9.07 grams to the litre was found to be isotonic with a benzil solution containing 0.0345 gram-molecule per litre, hence the molecular weight is 263.

A solution in ethylene dibromide containing 11.5 grams per litre was isotonic with a solution containing between 0.057 and 0.064 gram-molecule of triphenylmethane per litre. Hence molecular weight is 180—202, giving 191 as a mean value. A solution containing 12.7 grams per litre was isotonic with a solution containing between 0.055 and 0.066 gram-molecule of benzil per litre, hence the molecular weight is 192—231, the mean being 211.

The analyses and molecular weight determinations correspond best with the formula  $C_{16}H_{12}$ , and the properties of the hydrocarbon correspond fairly well with those of a hydrocarbon having this formula, which had already been prepared by several chemists.

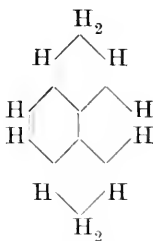
Liebermann and Dorp (*Annalen*, 1872, 163, 112), by the distillation of ruficoccin with zinc dust, obtained a hydrocarbon,  $C_{16}H_{12}$ , melting at  $183-188^\circ$ , and giving a quinone melting at  $250^\circ$ . The constitution

$C_{14}H_8 \begin{matrix} < CH_2 \\ & | \\ < CH_2 \end{matrix}$  is suggested by these authors for this hydrocarbon. By distilling either coccin or carmine with zinc dust, Fürth (*Ber.*, 1883, 16, 2169) obtained a hydrocarbon having this formula and melting at  $186-187^\circ$ .

Bischoff (*Ber.*, 1890, 23, 1905 and 3200), by the action of methyl chloride on naphthalene in the presence of aluminium chloride, obtained,

among other products, a hydrocarbon, boiling at about  $360^{\circ}$ , from which a crystalline substance was isolated having the empirical formula  $C_4H_3$  and melting at  $179-181^{\circ}$ .

The melting point and solubility of Bischoff's compound correspond exactly with those of the compound prepared by the authors. It may or may not be identical with the compound from ruficoccin. Bischoff put forward the following formula :



for his hydrocarbon, suggesting that it might be derived from 1 : 4 : 5 : 8-tetramethylnaphthalene.

Whatever the formula of the hydrocarbon may be, it is clear that unless the highly improbable assumption is made that some of the naphthalene molecules are partially broken down, and the hydrocarbon then built up from intact naphthalene molecules and the degradation products, it must be concluded that a carbon ring has been synthesised from carbon monoxide. The only other case in which this has been shown to occur is in the production of potassium hexaoxybenzene by the action of carbon monoxide on potassium.

*Reaction of Nickel Carbonyl with Benzene in the Presence of Aluminium Bromide.*

In this case, a reaction readily takes place, and the product was treated in the manner already described for aluminium chloride. No benzaldehyde and no anthracene could be detected, but a crystalline product distilling at  $300^{\circ}$  under 30 mm. pressure, and an uncrystallisable oil with a higher boiling point were obtained. The crystalline product, on repeated crystallisation from hot alcohol, was obtained in lustrous plates melting at  $181-181.5^{\circ}$ , and appeared to be identical in every respect with that obtained from naphthalene, a mixture of the two substances melting at  $181-181.5^{\circ}$ .

The authors desire to express their thanks to Dr. Mond for his aid in supplying the means for the conduct of these investigations.

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CAMBRIDGE.

## XXVIII.—*Optically Active Nitrogen Compounds. d- and l-Phenylbenzylmethylethylammonium Salts.*

By HUMPHREY OWEN JONES.

THE first definite proof of the existence of optically active compounds in which the optical activity is due to asymmetric atoms other than carbon atoms was given by Pope and Peachey (*Trans.*, 1899, **75**, 1127), when they resolved Wedekind's  $\alpha$ -phenylbenzylmethylallylammonium iodide into dextro- and ævo-rotatory forms in which the activity is caused by the asymmetry of the quinquivalent nitrogen atom. Up to the present time, the salts then described, together with those described later by Pope and Harvey (*Trans.*, 1901, **79**, 828), derived from the same substance, are the only active nitrogen compounds known.

The  $\alpha$ - and  $\beta$ -phenylbenzylmethylallylammonium salts are also unique in that they are the only ones which have been shown to exist in *definite* stable isomeric forms. The phenomena observed in the phenylmethylethylallylammonium iodides by Wedekind (*Ber.*, 1903, **36**, 3791), if they can be considered as due to isomerism at all, are of quite a different order, since the differences vanish when the compounds separate from solution and the amorphous product becomes crystalline. It becomes therefore a matter of importance to determine whether the existence of optical activity is in any way connected with the existence of isomerides or whether it is dependent on the presence of any special radicles.

The resolution of one of these compounds was undertaken by the author in order to show that the negative result of the attempts to prepare active forms of salts of the type  $\text{NR}'\text{R}''\text{R}_2'''\text{X}$  was not due to the absence of ordinary isomerides or to the particular radicles used. A preliminary notice of the partial resolution of phenylbenzylmethylethylammonium compounds has already been published (*Trans.*, 1903, **83**, 1419).

This subject acquired additional interest after the publication of a paper by Wedekind (*Zeit. physikal. Chem.*, 1903, **46**, 235), in which unsuccessful attempts to resolve two salts, namely, *p*-tolylbenzylmethylallylammonium and *p*-tolylmethylethylallylammonium *d*-camphorsulphonates, are described.

The question of the existence of isomerides of phenylbenzylethylmethylammonium iodide was first investigated by preparing this compound in the three possible ways and carefully comparing the properties of the products.

*Phenylbenzylmethylethylammonium Iodide.*

(1) A mixture of methylethylaniline (27 grams) and benzyl iodide (43 grams) in molecular proportion set almost completely to a solid gum in the course of about two hours. The gummy mass, when dissolved in rectified spirit, crystallised slowly; the crystals which separated were short, almost colourless prisms melting at  $139\text{--}140^\circ$ , the melting point being slightly raised by repeatedly crystallising the substance from alcohol. Unfortunately, with this compound, as with some of the other substituted ammonium salts previously investigated, the melting point is not a constant, but depends on the rate of heating, and was sometimes found to have been lowered a degree or two when the substance was left for some time in a stoppered tube, although in this case no visible change had taken place. The carefully purified salt, when slowly heated, becomes slightly brown at  $140^\circ$ , and melts either at, or just below,  $144\text{--}145^\circ$ . If, however, the tube containing the salt is not introduced until the bath is at about  $140^\circ$ , the salt may not melt below  $146\text{--}148^\circ$ . These differences are apparently due to partial decomposition below the melting point. Hence, in the comparison of melting points described below, two tubes containing the substances to be compared were always heated side by side in the same bath.

(2) Benzylethylaniline, which was prepared as described by Friedländer (*Ber.*, 1889, 22, 588) by the action of ethyl iodide on benzylaniline at  $100^\circ$ , boiled at  $286\text{--}288^\circ$  under 750 mm. and at  $190^\circ$  under 20 mm. pressure.

A mixture of this base (14.4 grams) with methyl iodide (10 grams) in molecular proportion gradually deposited the ammonium iodide in a crystalline form, yielding about 1.6 per cent. after three days. The cold alcoholic solution, when diluted with ether, slowly deposited prismatic crystals which melted at  $145^\circ$  when slowly heated and at  $147\text{--}148^\circ$  when quickly heated, or a little higher than the compound produced by method (1). A mixture of the two preparations melted at the same temperature as the product of the second method; moreover, the crystalline form of the two products is the same, so that the two are apparently identical.

(3) A mixture of benzylmethylaniline (19.6 grams) and ethyl iodide (15.6 grams) in molecular proportion deposited, with extreme slowness, a crystalline solid and a little gummy matter, not more than about 2 per cent. of the salt being obtained after about a fortnight. The melting point of the crude substance was  $135\text{--}137^\circ$ , and on recrystallisation from alcohol the melting point rose to  $143\text{--}144^\circ$ , being identical with that of the product from the first method; a mixture of the two melted at

the same temperature, so that they are evidently the same. The quantity of material available was insufficient to furnish crystals large enough for crystallographic examination.

Hence no definite stable isomerides can be produced in this way. It is possible that the gummy product produced at first by method (1) and also the amorphous phenylmethylethylallylammonium iodide of Wedekind (*Ber.*, 1903, 36, 3791) may represent the untransformed, and, in these cases, the unstable addition product, which, when deposited from solution, undergoes transformation into the more stable form, but which is stable under special conditions, as in the case of certain compounds investigated by Kipping, and the  $\alpha$ - and  $\beta$ -phenylbenzylmethylallylammonium compounds of Wedekind (compare *Trans.*, 1903, 83, 1405).

A specimen dried in a vacuum desiccator was employed in the following analysis:

0.1350 gave 0.2695  $\text{CO}_2$  and 0.0691  $\text{H}_2\text{O}$ .  $\text{C} = 54.4$ ;  $\text{H} = 5.60$ .

$\text{C}_{16}\text{H}_{20}\text{NI}$  requires  $\text{C} = 54.4$ ;  $\text{H} = 5.66$  per cent.

#### *Resolution of the d- and l-Camphorsulphonates.*

The camphorsulphonates were made in the usual manner by boiling the silver salt of the acid with the calculated quantity of the ammonium iodide prepared by method (1), and a mixture of ethyl acetate and a little alcohol. *l*-Camphorsulphonic acid was prepared from *l*-borneol as described by Pope and Harvey (*Trans.*, 1901, 79, 76) and was found to melt at  $193^\circ$ ; its ammonium salt in aqueous solution gave  $[\text{M}]_D = 51.5^\circ$ . The *l*-camphorsulphonate of the *l*-base was prepared both from the inactive iodide and from crude *l*-iodide obtained from the most soluble portions of the *d*-camphorsulphonate.

The camphorsulphonates crystallise readily, are very sparingly soluble in acetone and ethyl acetate, even when hot, but dissolve quite readily in methylene diethyl ether (ethylal); a mixture of this with ethyl acetate was therefore used as solvent. The crystallisation was carried out at a comparatively low temperature, as it was found that prolonged heating induced a distinct retrogression in the rotatory power of the salt, most probably due to racemisation. Several crystallisations (6—8) were found to be necessary before the rotatory power of the salts became constant; the resolution therefore proceeds somewhat slowly and is not effected quite so readily as in the case of the phenylbenzylmethylallylammonium salts resolved by Pope and Peachey (*loc. cit.*).

The rotatory power of the salts is small compared with that of the last-mentioned compounds, so that on this account a much larger quantity of material must be worked up (about 30—40 grams of the

camphorsulphonates were employed), so that for this reason, and on account of the slight solubility of the salts and the necessity for keeping down the temperature, the process is somewhat tedious. The amount of the rotation observed was in all cases small even with comparatively concentrated solutions, consequently the experimental error is necessarily large, and great care had to be exercised in order to secure the highest degree of accuracy.

*d-Phenylbenzylmethylethylammonium d-Camphorsulphonate.*

This salt formed lustrous, prismatic crystals melting sharply at  $180-181^{\circ}$ ; its rotatory power in aqueous solution was determined several times during the process of fractional crystallisation, and  $[M]_D$  was found to approach a constant value of about  $71^{\circ}$ . A specimen was then dissolved in a mixture of ethyl acetate and ethylal, the solution allowed to evaporate slowly in a desiccator, and the successive fractions examined. The identity of the two results given below shows, within the limits of experimental error, that the compound is pure.

First fraction: 1.086 in 25 c.c. gave  $\alpha_D = 1.35^{\circ}$  in a 200 mm. tube,\* hence  $[\alpha]_D = 15.54^{\circ}$  and  $[M]_D = 71.0^{\circ}$ .

Third fraction: 1.063 in 25 c.c. gave  $\alpha_D = 1.32^{\circ}$ , hence  $[\alpha]_D = 15.52^{\circ}$  and  $[M]_D = 70.94^{\circ}$ .

0.1355 gave 0.3385  $\text{CO}_2$  and 0.0935  $\text{H}_2\text{O}$ .  $\text{C} = 68.1$ ;  $\text{H} = 7.7$ .

$\text{C}_{26}\text{H}_{35}\text{O}_4\text{NS}$  requires  $\text{C} = 68.2$ ;  $\text{H} = 7.6$  per cent.

*l-Phenylbenzylmethylethylammonium l-Camphorsulphonate.*

The salt has exactly the same properties as the corresponding *dd*-salt, crystallising in similar lustrous prisms and melting at  $180-181^{\circ}$ ; its molecular rotatory power in aqueous solution gradually became constant at about  $71^{\circ}$ . A specimen was then dissolved in a mixture of ethyl acetate and ethylal, the solution allowed to evaporate slowly in a desiccator, and the rotatory power of the successive fractions examined. The practical identity of the numbers obtained with one another and with those already given for the dextrorotatory isomeride shows that the salt is homogeneous.

First fraction: 0.583 in 25 c.c. gave  $\alpha_D = -0.73^{\circ}$ , hence  $[\alpha]_D = -15.6^{\circ}$  and  $[M]_D = -71.5^{\circ}$ .

Second fraction: 1.027 in 25 c.c. gave  $\alpha_D = -1.27^{\circ}$ , hence  $[\alpha]_D = -15.46^{\circ}$  and  $[M]_D = -70.7^{\circ}$ .

\* All the following determinations of  $\alpha_D$  were carried out in a 200 mm. tube.

Third fraction: 1.076 in 25 c.c. gave  $\alpha_D = -1.33^\circ$ , hence  $[\alpha]_D = -15.45^\circ$  and  $[M]_D = -70.6^\circ$ .

Fourth fraction: 1.002 in 25 c.c. gave  $\alpha_D = -1.27^\circ$ , hence  $[\alpha]_D = -15.8^\circ$  and  $[M]_D = -72.3^\circ$ .

0.1930 gave 0.4829  $\text{CO}_2$  and 0.1330  $\text{H}_2\text{O}$ . C = 68.2; H = 7.66.

$\text{C}_{26}\text{H}_{35}\text{O}_4\text{NS}$  requires C = 68.2; H = 7.6 per cent.

The molecular rotatory power of the *d*-phenylbenzylmethylethylammonium *d*-camphorsulphonate is therefore  $+71.0^\circ$  (mean), and that of the corresponding *l*-salt is  $-71.2^\circ$  (mean). Since the molecular rotatory powers of the *d*- and *l*-camphorsulphonate ions are respectively  $+51.7^\circ$  and  $-51.6^\circ$ , the molecular rotatory powers of the *d*- and *l*-phenylbenzylmethylethylammonium ions are  $+19.3^\circ$  and  $-19.6^\circ$  respectively. The value for the *d*-phenylbenzylmethylethylammonium *d*-camphorsulphonate agrees fairly well with that already given, namely,  $+69^\circ$  (*loc. cit.*, 1419). The molecular rotatory powers of the *d*- and *l*-phenylbenzylmethylallylammonium ions are  $+166.4^\circ$  and  $-159^\circ$  respectively (Pope and Harvey, *loc. cit.*).

The remarkably low value obtained for these compounds, which only differ from those last mentioned by the introduction of an ethyl instead of an allyl radicle, is therefore very surprising. It is difficult to see why such a small difference as this could produce such an enormous change in the rotatory powers were it not that it has been repeatedly shown that an ethylene linking exerts a very marked influence in increasing the rotatory power. An attempt was made to confirm these values by the examination of the bromocamphorsulphonates, but unfortunately these have not been obtained crystalline. Even when the *d*-iodide of the base, obtained from the *d*-camphorsulphonate, was converted into the *d*-bromocamphorsulphonate, the salt still remained a gum and could not be induced to crystallise.

#### *d*-Phenylbenzylmethylethylammonium Iodide.

The *d*-iodide of the base was obtained in a crystalline form by adding the calculated quantity of a concentrated aqueous solution of potassium iodide to an aqueous solution of the *d*-camphorsulphonate. The crystalline salt thus obtained, dried in a vacuum desiccator, was found to melt at practically the same temperature as the inactive iodide, admixture with which did not appreciably change the melting point.

The specimen for analysis was crystallised from cold alcohol in the dark.

0.1334 gave 0.2655  $\text{CO}_2$  and 0.0700  $\text{H}_2\text{O}$ . C = 54.28; H = 5.82.

$\text{C}_{16}\text{H}_{20}\text{NI}$  requires C = 54.39; H = 5.66 per cent.

The determinations of the rotatory power of the iodide offer considerable difficulties. The salt has a very small rotatory power and is very sparingly soluble in alcohol, so that, even with practically saturated solutions, the rotations observed were very small, for example,  $0.3-0.4^\circ$ , and hence the experimental error is very large. Chloroform dissolves a little more of the salt, but the solution shows a peculiar supersaturation phenomenon, the salt first dissolves and then partly crystallises out, in most cases rapidly, but sometimes more slowly, leaving a solution which gives a rotation of about the same magnitude as that of an alcoholic solution. Racemisation also occurs slowly in a chloroform solution, and consequently its use was abandoned.

Several determinations were made in alcoholic solution at a concentration of about 2 per cent., which represents a nearly saturated solution at the ordinary temperature. The following data represent three of these determinations:

0.5620 in 25 c.c. absolute alcohol gave  $\alpha_D = 0.37^\circ$ , hence  $[\alpha]_D = 8.23^\circ$  and  $[M]_D = 29.0^\circ$ .

0.5455 in 25 c.c. gave  $\alpha_D = 0.36^\circ$ , hence  $[\alpha]_D = 8.25^\circ$  and  $[M]_D = 29.1^\circ$ .

0.5560 in 25 c.c. gave  $\alpha_D = 0.38^\circ$ , hence  $[\alpha]_D = 8.5^\circ$  and  $[M]_D = 30.1^\circ$ .

It may therefore be concluded that the value of  $[\alpha]_D$  for the *d*-iodide is about  $8.3^\circ$ , although no very great reliance can be placed on these numbers owing to the very large experimental error.

#### *1-Phenylbenzylmethylethylammonium Iodide.*

This iodide was prepared from the corresponding camphorsulphonate in the manner already described for the *d*-iodide. The salt, after recrystallisation from cold alcohol in the dark, was found to melt, when slowly heated, at the same temperature as the *l*- and *d*-iodides, and mixtures of the *l*- and inactive iodides also melted at the same temperature.

The following analysis was made on a specimen dried in a vacuum desiccator.

0.1862 gave 0.3701  $\text{CO}_2$  and 0.0975  $\text{H}_2\text{O}$ .  $\text{C} = 54.2$ ;  $\text{H} = 5.81$ .

$\text{C}_{16}\text{H}_{20}\text{NI}$  requires  $\text{C} = 54.39$ ;  $\text{H} = 5.66$  per cent.

The rotatory power was determined in alcoholic solution in the same way as that of the *d*-iodide, with the following results:

0.547 in 25 c.c. absolute alcohol gave  $\alpha_D = -0.38^\circ$ , hence  $[\alpha]_D = -8.68^\circ$  and  $[M]_D = -30.8^\circ$ .

0.514 in 25 c.c. absolute alcohol gave  $\alpha_D = -0.34^\circ$ , hence  $[\alpha]_D = -8.27^\circ$  and  $[M]_D = -29.2^\circ$ .

0.526 in 25 c.c. absolute alcohol gave  $\alpha_D = -0.35^\circ$ , hence  $[\alpha]_D = -8.32^\circ$  and  $[M]_D = -29.4^\circ$ .

The specific rotatory power of the *l*-iodide in alcoholic solution is therefore numerically identical, within the limits of experimental error, with that of the corresponding *d*-salt, namely, about  $-8.4^\circ$ .

*Autoracemisation of the Phenylbenzylmethylethylammonium Salts.*

The camphorsulphonates retain their rotatory power practically unchanged for weeks in aqueous solution and also in cold alcoholic or ethylal solutions. If, however, the solutions are heated, the aqueous solution becomes turbid, the rotatory power of the other solutions diminishes, and the salt deposited from them has a distinctly low rotatory power. In one experiment, a specimen of *d*-phenylbenzylmethylethylammonium *d*-camphorsulphonate, having  $[M]_D = 71.4^\circ$ , was recrystallised from a hot mixture of ethyl acetate and acetone, the solution being heated for about 10 minutes in order to bring all the salt into solution; the salt which was deposited on cooling had a much lower rotatory power, namely,  $[M]_D = 56.0^\circ$ . Boiling in ethyl acetate solution had therefore caused almost complete racemisation of the basic part of the molecule.

In the fractional crystallisation of these salts, it is consequently necessary to avoid heating the solutions, and in practice the temperature was usually not raised above about  $40^\circ$ . The solutions of the iodides in alcohol retain their rotatory power in the cold for a long time, especially when left in the dark. On heating, however, the rotatory power diminishes, so that when recrystallising these compounds from alcohol the process must be carried out at as low a temperature as possible. In chloroform solution, racemisation takes place slowly in the cold and in absence of light.

On one occasion, a fairly strong chloroform solution of the *d*-iodide (not quite pure), when put into the tube, did not deposit the excess of iodide as all other chloroform solutions did, and was observed to be in the supersaturated state for about a week. The rest of the solution in the flask soon deposited crystals just as the other chloroform solutions had done.

0.859 in 25 c.c. chloroform gave  $\alpha_D = 0.64^\circ$ , hence  $[\alpha]_D = 9.31^\circ$ ;  $[M]_D = 33.8^\circ$ .

The rotatory power diminished gradually at first at the rate of about  $0.1^\circ$  per day, until it became practically inactive after a little more than a week. These salts therefore behave much in the same way as

the  $\alpha$ -phenylbenzylmethylallylammonium salts investigated by Pope and Harvey (*loc. cit.*).

The effect of chloroform in causing racemisation may be due, as suggested by these authors, to a dissociation of the ammonium salt into the tertiary amine and alkyl iodide and subsequent recombination to form the quaternary compound. This hypothesis is supported by an experiment made by the authors, which showed that the rate of formation of the salt in chloroform solution is large compared with that in alcohol or ether. Wedekind (*Zeit. physikal. Chem.*, 1900, 6, 23), on determining the molecular weight of the iodide in chloroform solution by the ebullioscopic method, obtained values about one-third of the calculated value indicating dissociation of the salt into its constituents.

It is difficult to see how the iodide could dissociate into three substances, the results therefore seem to indicate that the ebullioscopic method is inapplicable here. Moreover, the slow rate of racemisation indicates dissociation to a slight extent only; were the dissociation complete, the racemisation ought to be instantaneous.

The molecular weights of phenylbenzylmethylallylammonium iodide and phenylbenzylmethylethylammonium iodide in chloroform solution were determined by Mr. G. Barger, B.A., of King's College, who used his microscopic method. The author is glad to take the opportunity of expressing his thanks to Mr. Barger for the care and trouble which he expended on these determinations (compare this vol., p. 286).

#### *Phenylbenzylmethylethylammonium Iodide.*

A solution containing 23.9 grams per litre was found to be isotonic with a solution of triphenylmethane containing 0.075 gram-molecule per litre, whence the molecular weight is 319. A solution containing 25.1 grams per litre was found to be isotonic with a solution of azobenzene containing 0.0725 gram-molecule per litre, which gives a molecular weight 346. The calculated molecular weight is 353, so that at the ordinary temperature the molecular weight is approximately normal.

#### *$\alpha$ -Phenylbenzylmethylallylammonium Iodide.*

This salt, being much more soluble in chloroform than the foregoing compound, gives better results. A solution containing 59.0 grams per litre was found to be isotonic with a solution of triphenylmethane containing 0.16—0.17 gram-molecule per litre. Hence the molecular weight of the iodide lies between 335 and 381 (mean 358). The calculated value for  $C_{17}H_{20}NI$  is 365. So that the molecular

weight at the ordinary temperature gives no indication of extensive dissociation.

A peculiar phenomenon was observed in the case of both salts, which was, however, more marked with the phenylbenzylmethylallyl-ammonium iodide than with the other. In the freshly prepared solution, the molecular weight always appeared slightly too high; it then gradually diminished, became normal, and went on diminishing until it was somewhat too low. The rate of diminution was much increased by raising the temperature. This behaviour is being investigated, as it may throw light on the cause of the racemisation, and is probably the cause of the anomalous results obtained by the ebullioscopic method.

The above results, which show that in both cases there is only a very slight dissociation of the salts in chloroform solution at the ordinary temperature, thus account for the slow rate of racemisation.

*i*-Phenylbenzylmethylethylammonium Bromide.—This salt was prepared from the iodide by digesting an alcoholic solution with silver bromide. It crystallises from alcohol in prisms closely resembling those of the iodide, which melt sharply at 155–156°. The melting point of the bromide does not depend on the rate of heating in the same way as the iodide.

*l*-Phenylbenzylmethylethylammonium bromide is not precipitated from the aqueous solution of the camphorsulphonate by the addition of a concentrated aqueous solution of potassium bromide, and consequently had to be prepared by the same method as the inactive compound. It crystallises from alcohol in long prisms melting at 155–156°. A mixture of the *l*- and *i*-bromides also melts sharply at the same temperature.

A determination of the rotatory power in alcoholic solution was made with the following result:

0.634 in 25 c.c. gave  $\alpha_D = -0.68^\circ$ ; hence  $[\alpha]_D = -13.4^\circ$  and  $[M]_D = -41.1^\circ$ .

The rotatory power is greater than that of the corresponding iodide, just as the rotatory power of the active  $\alpha$ -phenylbenzylmethylallyl-ammonium bromide is greater than that of the iodide. The rotatory power of the bromide diminishes on recrystallising from alcohol.

0.212 gave 0.4850 CO<sub>2</sub> and 0.1200 H<sub>2</sub>O. C = 62.36; H = 6.4.

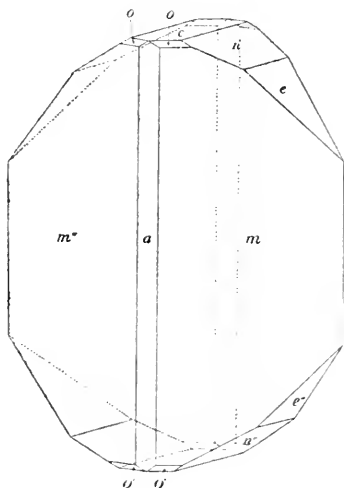
C<sub>16</sub>H<sub>20</sub>NBr requires C = 62.7; H = 6.53 per cent.

*Crystalline Form of the d-, l-, and i-Phenylbenzylmethylethylammonium Iodides.*

The crystallographic examination was undertaken in order to decide whether the inactive form was a racemic compound or merely an inactive mixture. These salts crystallise from alcoholic solutions in beautiful, lustrous prisms, the faces of which, although appearing quite bright, nevertheless give bad reflections on a goniometer, so that it was found difficult to get good measurements. The crystals could only be obtained of very small size, 1—2 mm. in length, and were therefore troublesome to measure.

The dominant form was always the prism  $m\{110\}$ , the pinacoid

FIG. 1.

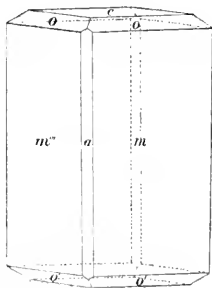


$a\{100\}$  was sometimes present as a very narrow face, but  $b\{010\}$  was never observed. Two distinct types of crystals were observed, see Figs. 1 and 2, one sort exhibited the domes  $e\{011\}$  and  $n\{012\}$  with the basal plane  $c\{001\}$ , often as a mere line, and  $o\{112\}$  was sometimes present; the other kind showed a well-developed basal plane and no domes, but  $o\{112\}$  was always present, and  $a\{100\}$  was occasionally observed. No general forms were present, so that the question of hemihedrism could not be definitely settled. From analogy with the  $\alpha$ -phenylbenzylmethylallylammonium salts and the phenylmethylethylallylammonium salts which belong to the sphenoidal class of the prismatic system, it is probable that this salt also belongs to the same class;

this is supported by the scanty evidence which was obtained by examining the etched figures produced on the faces  $m\{110\}$  and  $m'''\{1\bar{1}0\}$  by dilute alcohol. The few definite figures observed were devoid of a plane of symmetry, and those on  $m$  and  $m'''$  were interchangeable by rotation about the dyad axis.

The crystals of the *d*-, *l*-, and *i*-salts are similar in habit and appearance and have identical angles, so that the inactive salt is either an inactive mixture or a pseudoracemic compound. The fact

FIG. 2.



of the melting points of mixtures of *d*- or *l*-salt with the *i*-salt being the same as that of any one of the salts also supports this conclusion.

Crystalline system. Prismatic. Sphenoidal Class (?).

$$a : b : c = 0.7456 : 1 : 1.1409.$$

Forms observed:  $a\{100\}$ ,  $m\{110\}$ ,  $c\{001\}$ ,  $e\{011\}$ ,  $n\{012\}$ , and  $o\{112\}$ .

The following angular measurements were made:

Angle.	Number of observations.	Limits.	Mean.	Calculated.
$m\ m''' = 110 : 1\bar{1}0$	20	73° 0' — 73° 55'	73° 25'	—
$m\ m' = 110 : \bar{1}10$	19	106 0 — 106 50	106 34	106° 35'
$a\ m = 100 : 110$	4	36 20 — 36 55	36 40	36 37
$c\ c = 001 : 011$	10	48 35 — 48 56	48 46	—
$c\ n = 001 : 012$	10	29 19 — 29 56	29 37	29 42
$e\ e' = 011 : 0\bar{1}1$	6	97 14 — 97 46	97 32	97 32
$n\ n' = 012 : 0\bar{1}2$	4	58 50 — 59 50	59 12	59 34
$c\ n = 011 : 012$	8	18 25 — 19 20	19 0	19 4
$c\ n' = 011 : 0\bar{1}2$	7	78 10 — 78 56	78 28	78 28
$m\ n = 110 : 012$	3	72 40 — 73 30	73 13	73 3
$m''\ n = 1\bar{1}0 : 012$	3	106 39 — 107 20	106 56	106 57
$c\ o = 001 : 112$	9	20 20 — 21 19	20 56	20 58
$m\ o = 110 : 112$	10	69 0 — 69 30	69 14	69 8

The author desires to express his thanks to Mr. A. Hutchinson for kindly placing at his disposal the goniometer with which the above measurements were made.

It may therefore be concluded that (1) the ammonium compounds of the type  $\text{NR}'\text{R}''\text{R}'''\text{R}''''\text{X}$  can be resolved into enantiomorphously related optically active forms, although the resolution may often be difficult owing to the feeble rotatory power of the salts and the ease with which racemisation takes place, and that (2) the existence of optical activity is independent of the existence of ordinary isomerides of the salt.

Racemisation of the active salts takes place very readily on heating or on allowing solutions in chloroform to remain in the cold; the cause of the racemisation is probably dissociation into tertiary amine and alkyl iodide, followed rapidly by recombination, as suggested by Pope and Harvey.

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XXIX.—*Diortho-substituted Benzoic Acids. Part V.*  
*Formation of Salts from Diortho-substituted Benzoic*  
*Acids and Organic Bases.*

By JOHN JOSEPH SUDBOROUGH and WILLIAM ROBERTS.

IN a previous communication on this subject (Lloyd and Sudborough, *Trans.*, 1899, 75, 580), it has been shown that stereochemical influences only slightly affect the reactions between substituted benzoic acids and organic bases, these influences being completely masked by the effect of the comparative strengths of the acids and bases. Since the publication of this earlier paper, Emil Fischer (*Ber.*, 1900, 33, 345, 1967) has drawn attention to the fact that diortho-substituted tertiary bases are incapable of combining with an alkyl iodide to yield quaternary ammonium compounds. As the earlier experiments were not carried out with bases of this type, we have tried to prepare salts from diortho-substituted alkylated arylamines of the type of dimethyl-

mesidine and various substituted benzoic acids, including those with two ortho-substituents. We have also attempted to combine the same acids with diethyl- $\alpha$ - and  $\beta$ -naphthylamines.

*s*-Trinitrobenzoic acid forms salts with all the bases examined; 2:4:6-tribromo-3-aminobenzoic acid also forms salts with a number of the bases, but not many have been obtained in a crystalline form. It would thus appear that the introduction of ortho-substituents into the acid and basic molecules does not prevent the formation of salts, provided that the acid is very strong and the base not too weak.

In addition, we have attempted to settle a point raised in the earlier paper (*ibid.*, p. 583), namely, the behaviour of various organic bases towards a weak diortho-substituted acid of the type of *s*-trimethylbenzoic acid. The acid forms a well-defined, crystalline salt with a strong base such as benzylamine, and also dissolves readily in 33 per cent. aqueous trimethylamine solution, but all attempts to combine it with tertiary bases such as dimethylmesidine, dimethyl- $\psi$ -cumidine, bromodimethyl-*m*-xylylidine, and diethylaniline have given negative results; in each case, the unaltered acid crystallised out from the different solvents, even when two or three times the theoretical amount of base was employed. It is clear that the loss of the function of salt formation is not due to the presence of ortho-substituents in the basic molecules, because a simple base like diethylaniline is incapable of forming a salt with this acid. In order to determine whether it is due to ortho-substituents in the acid molecule, we have endeavoured to prepare salts from the same bases and mono-substituted benzoic acids containing substituent methyl, bromo-, and nitro-groups. The fact that no salts are formed from either *m*-toluic acid and dimethylaniline, or *p*-toluic acid and dimethylaniline or  $\psi$ -cumidine indicate that the presence of ortho-substituents in the acid molecule is not necessary in order to inhibit salt formation.

In addition to the normal salts formed by the union of one molecule of acid with one of the base, we have obtained a number of acid salts formed by the union of two molecules of acid with one of the base, as, for example, the acid salts derived from  $\psi$ -cumidine and *o*-toluic acid, dimethyl- $\psi$ -cumidine and *m*-nitrobenzoic acid,  $\psi$ -cumidine and *m*-nitrobenzoic acid, dimethyl- $\psi$ -cumidine and tribromoaminobenzoic acid, and dimethyl- $\psi$ -cumidine and *o*-nitrobenzoic acid. These compounds are similar to the acid potassium and ammonium salts derived from substituted benzoic acids, which have been recently described by Farmer (*Trans.*, 1903, 83, 1440). According to this investigator, the probable constitution of these acid salts is represented by the formula  $\begin{array}{c} \text{R}-\text{CO} \\ \text{R}\cdot\text{CO}\cdot\text{O} \end{array} > \text{O} < \begin{array}{c} \text{K} \\ \text{H} \end{array}$ , and the molecule contains a quadrivalent oxygen atom. With such a formula, it is quite possible that inhibition

through stereochemical influences should occur. If ortho-substituents retard or prevent the formation of additive compounds involving the carbonyl residue of the substituted benzoic acid (compare *Trans.*, 1899, **75**, 581), it is quite possible that ortho-substituents would also prevent the conversion of the bivalent oxygen atom of the hydroxyl group into a quadrivalent oxygen. We might therefore expect that diortho-substituted benzoic acids would not give rise to acid salts. Although we have not particularly investigated this question, we have met with only one such salt derived from dimethyl- $\psi$ -cumidine and tribromoaminobenzoic acid.

The salts were usually analysed by determining the amount of acid present according to the method previously described (*loc. cit.*, 584). We have found that the majority of the salts can also be analysed by titrating their alcoholic solutions with standard baryta when phenolphthalein is used as indicator. The presence of the organic base does not interfere with the titration, and good results are obtained. For example, 20 c.c. of *N*/20 oxalic acid required 15.4 c.c. of baryta solution, and 20 c.c. of *N*/20 oxalic acid mixed with 6 drops of dimethyl- $\psi$ -cumidine also required 15.4 c.c. of the same alkali solution.

## EXPERIMENTAL.

### A. Preparation of Bases.

Dimethyl- $\psi$ -cumidine,  $C_6H_2Me_3 \cdot NMe_2$  [ $Me_3 : NMe_2 = 2 : 4 : 5 : 1$ ], was obtained by a method somewhat similar to that employed by Noelting in the preparation of dimethyl-*m*-xylidine (*Ber.*, 1891, **24**, 563); 20 grams of  $\psi$ -cumidine melting at 68°, 70 grams of methyl iodide, 47 grams of sodium carbonate, and 500 grams of water were heated in a reflux apparatus until all the iodide had disappeared; caustic potash solution was added and the base extracted with ether. The ethereal solution, when dry, gave 17 grams of a colourless oil distilling at 219°, which was characterised by the formation of its *platinichloride*.

0.3808 gave 0.1003 Pt = 26.47.

$(C_6H_2Me_3 \cdot NMe_2)_2, H_2PtCl_6$  requires 26.47 per cent.

Dimethylmesidine [ $Me_3 : NMe_2 = 2 : 4 : 6 : 1$ ], obtained in a similar manner from mesidine, was freed from secondary base by heating in a sealed tube with methyl iodide and dry magnesia at 100° (*Fischer, Ber.*, 1900, **33**, 1968).

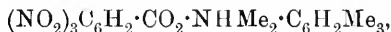
Bromo-*m*-xylidine [ $Me_2 : NH_2 : Br = 2 : 4 : 1 : 6$ ], melting at 46–47°, was obtained by Fischer's method (*ibid.*, 1971) and transformed into the tertiary base by the method employed in the case of mesidine.

Diethyl  $\alpha$ - and  $\beta$ -naphthylamines were prepared by Morgan's

process (Trans., 1900, 77, 823). Of the acids employed, the 2:4:6-tribromo-3-aminobenzoic acid was prepared by the method already described (Trans., 1899, 75, 589), the *s*-trinitrobenzoic acid was kindly presented by the Chemische-Fabrik Griesheim, and the *s*-trimethylbenzoic acid was prepared from mesitylglyoxylic acid (Meyer, *Annalen*, 1888, 246, 139). Van Scherperzeil (*Rec. trav. chim.*, 1900, 19, 380) recommends heating the glyoxylic acid with concentrated sulphuric acid until no more carbon monoxide is evolved, but we find that in order to obtain a good yield the temperature should be carefully regulated, the best yields being obtained when the temperature is kept about 40°; above 50°, carbon dioxide begins to be evolved, and the trimethylbenzoic acid itself is destroyed. In one experiment, we obtained 2.05 grams of trimethylbenzoic acid from 2.5 grams of the glyoxylic acid (m. p. 152°). The magenta coloration produced when glyoxylic acid is dissolved in concentrated sulphuric acid is extremely characteristic.

#### B. Salts from *s*-Trinitrobenzoic Acid.

*Dimethyl-ψ-cumidine 2:4:6-Trinitrobenzoate*.—The salt,



slowly separated in the form of snow-white, small needles on mixing alcoholic solutions of the acid and base; it crystallises from benzene in small needles, dissolves in hot water, alcohol, or chloroform, but is insoluble in carbon disulphide or light petroleum. Like the salts of trinitrobenzoic acid already described, it has no definite melting point; on heating, it melts and decomposes, yielding a dark red oil; the temperature at which this occurs varies considerably with the rate of heating. When heated fairly rapidly, it begins to turn dark at 115° and melts at 120°.

0.7179 gave 0.438 trinitrobenzoic acid = 61.0.

$\text{C}_{18}\text{H}_{20}\text{O}_8\text{N}_4$  requires 61.2 per cent.

*Dimethylmesidine Trinitrobenzoate*,  $(\text{NO}_2)_3\text{C}_6\text{H}_2\cdot\text{CO}_2\cdot\text{NHMe}_2\cdot\text{C}_6\text{H}_2\text{Me}_3$ .—The salt, obtained in the form of small needles when alcoholic solutions of the two components were mixed, begins to darken at 105°, and is completely decomposed at 116—117°; it dissolves in the ordinary solvents on heating, but is decomposed by some of these, more especially water or alcohol. When boiled for a short time with alcohol, it yields crystals melting at 122°; these proved to be *s*-trinitrobenzene, as with diethyl-β-naphthylamine they furnished purplish-black needles melting at 115—116°.

0.8867 gave 0.5392 trinitrobenzoic acid = 60.8.

$\text{C}_{18}\text{H}_{20}\text{O}_8\text{N}_4$  requires 61.2 per cent.

*Bromo-m-xylylidine Trinitrobenzoate*,  $(\text{NO}_2)_3 \cdot \text{C}_6\text{H}_2 \cdot \text{CO}_2 \cdot \text{NH}_3 \cdot \text{C}_6\text{H}_2\text{Me}_2\text{Br}$ .  
 —This salt, which was prepared by mixing alcoholic solutions of the acid and base, slowly separated in yellow, prismatic crystals which begin to change colour at  $130^\circ$ , are completely decomposed at  $150^\circ$ ; it is soluble in warm alcohol.

0.7154 gave 0.3986 trinitrobenzoic acid = 55.6.

$\text{C}_{15}\text{H}_{13}\text{O}_8\text{N}_4\text{Br}$  requires 56.2 per cent.

When the alcoholic solution was boiled for a short time, it acquired a red colour, and small, red needles melting at  $104\text{--}105^\circ$  were obtained on cooling. This substance, which is the additive compound,  $\text{C}_6\text{H}_2\text{Me}_2\text{Br} \cdot \text{NH}_2, \text{C}_6\text{H}_3(\text{NO}_2)_3$ , was also obtained by mixing alcoholic solutions of bromo-*m*-xylylidine and trinitrobenzene.

0.3824 gave 0.1955 trinitrobenzene = 51.1.

$\text{C}_{14}\text{H}_{13}\text{O}_6\text{N}_4\text{Br}$  requires 51.5 per cent.

It dissolves readily in ether, benzene, chloroform, and warm alcohol.

*Bromodimethyl-m-xylylidine Trinitrobenzoate*,

$(\text{NO}_2)_3 \cdot \text{C}_6\text{H}_2 \cdot \text{CO}_2 \cdot \text{NHMe}_2 \cdot \text{C}_6\text{H}_2\text{Me}_2\text{Br}$ .

—The salt, which was obtained from alcoholic solutions, begins to change colour at  $105^\circ$ , and is completely decomposed at  $108^\circ$ .

0.6506 gave 0.3435 trinitrobenzoic acid = 52.8.

$\text{C}_{17}\text{H}_{17}\text{O}_8\text{N}_4\text{Br}$  requires 53.0 per cent.

*Diethyl- $\alpha$ -naphthylamine s-Trinitrobenzoate*.—This salt separated in the form of flat, slightly yellow plates when warm alcoholic solutions of the acid and base were mixed. The mother liquor, when kept for several days, deposited bright red needles melting at  $95^\circ$ . These consist of diethyl- $\alpha$ -naphthylamine-trinitrobenzene (Trans., 1903, 83, 1338), and if the alcoholic solution of the salt is boiled, it is completely converted into this compound.

The salt decomposes at  $117\text{--}118^\circ$  and dissolves in alcohol, benzene, or chloroform.

0.5420 gave 0.3024 trinitrobenzoic acid = 55.8.

$\text{C}_{21}\text{H}_{20}\text{O}_8\text{N}_4$  requires 56.3 per cent.

*Diethyl- $\beta$ -naphthylamine s-Trinitrobenzoate*.—This salt, which was also obtained from alcoholic solutions of the acid and base, begins to darken at  $125^\circ$  and is completely decomposed at  $132^\circ$ ; it dissolves in hot water, alcohol, benzene, and chloroform, and, like its isomeride, shows a tendency to lose carbon dioxide and to form diethyl- $\beta$ -naphthylamine-trinitrobenzene melting at  $116^\circ$  (Trans., 1903, 83, 1340). This transformation is practically quantitative when an alcoholic solution of the salt is boiled for a short time.

0.4736 gave 0.2641 trinitrobenzoic acid = 55.7.

$C_{21}H_{20}O_8N_4$  requires 56.3 per cent.

The changes which these salts undergo when their alcoholic solutions are boiled, illustrate remarkably well the difference in stability between the additive compounds of *s*-trinitrobenzene with aniline derivatives and those produced with naphthylamine derivatives.

Dimethyl- $\psi$ -cumidine and dimethylmesidine, when boiled in alcoholic solution, yield the free base and *s*-trinitrobenzene, whereas diethyl- $\alpha$ - or - $\beta$ -naphthylamine trinitrobenzoate yields the corresponding coloured additive compound of the base with *s*-trinitrobenzene.

In order to determine whether dimethyl- $\psi$ -cumidine forms a definite compound with *s*-trinitrobenzene, we have made a number of experiments with different solutions, but in all cases, even when excess of the base was employed, crystals of unaltered *s*-trinitrobenzene were deposited. A coloured compound, obtained by crystallising *s*-trinitrobenzene from the base and allowing the crystals to dry in a desiccator containing a little of the free base, separated in small, bright red needles with no definite melting point, as when warmed they readily give up the base, leaving a colourless residue. When exposed to the air, the substance readily leaves a colourless residue of *s*-trinitrobenzene.

0.5 gave 0.2831 trinitrobenzene (m. p.  $122^\circ$ ) = 56.62.

$C_{17}H_{20}O_6N_4$  requires 56.6 per cent.

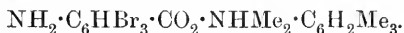
An additive compound of trinitrobenzene and  $\psi$ -cumidine, obtained by mixing together alcoholic solutions of the constituents, crystallises in long, slender, purple-brown needles melting at  $115^\circ$ , and is much more stable than the compound of aniline with trinitrobenzene.

0.3036 gave 41.3 c.c. moist nitrogen at  $17^\circ$  and 765 mm.  $N = 15.9$ .

$C_{15}H_{16}O_6N_4$  requires 16.09 per cent.

#### C. *Salts from 2:4:6-Tribromo-3-aminobenzoic Acid.*

*Dimethylmesidine 2:4:6-Tribromo-3-aminobenzoate,*

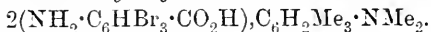


—The salt was obtained by dissolving the acid in ether, adding a slight excess of dimethylmesidine, and allowing the greater part of the ether to evaporate; it crystallised from water in small needles, softening at  $147^\circ$  and melting at  $163$ — $165^\circ$ .

0.8002 gave 0.5677 tribromoaminobenzoic acid = 70.9.

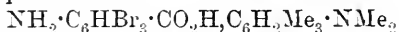
$C_{18}H_{21}O_2N_2Br_3$  requires 69.6 per cent.

The salt readily dissolves in alcohol, and also to a less extent in ether, benzene, chloroform, or hot water, but is very sparingly soluble in light petroleum.

*Dimethyl-ψ-cumidine Hydrogen Tribromoaminobenzoate,*

—When the acid and base were mixed in molecular proportion, the mixture did not set to a solid mass, but remained pasty, and when the mixture was crystallised from benzene, in which it is only moderately soluble, nodular aggregates of small, colourless needles melting at  $145.5$ — $146^\circ$  were obtained. When titrated in alcoholic solution with standard baryta, using phenolphthalein as indicator,  $0.4062$  required  $17.85$  c.c. of  $N/20 \text{ Ba(OH)}_2$ .

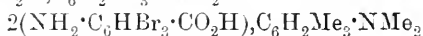
The amount required for the normal and acid salts,



and  $2(\text{NH}_2 \cdot \text{C}_6\text{HBr}_3 \cdot \text{CO}_2\text{H}), \text{C}_6\text{H}_2\text{Me}_3 \cdot \text{NMe}_2$ , are  $15.48$  and  $17.84$  c.c. respectively.

When decomposed with dilute hydrochloric acid and extracted with ether,  $0.6024$  gave  $0.505$  tribromoaminobenzoic acid =  $83.8$  per cent.

$\text{NH}_2 \cdot \text{C}_6\text{HBr}_3 \cdot \text{CO}_2\text{H}, \text{C}_6\text{H}_2\text{Me}_3 \cdot \text{NMe}_2$  and



require  $69.6$  and  $82.1$  per cent. respectively.

The same compound, obtained in the form of glistening, well-developed prisms by dissolving molecular quantities of the acid and base in alcohol, adding water, and allowing the solvent to evaporate slowly, melted at  $146^\circ$ .

$0.3$  required  $13.24$  c.c. of  $N/20 \text{ Ba(OH)}_2$  for neutralisation;  $2$  mols. acid +  $1$  mol. base requires  $13.17$  c.c.

The melting point was not affected by crystallisation from benzene.

We have attempted to prepare the normal salt ( $1$  mol. acid +  $1$  mol. base) by dissolving a mixture of the acid with twice its weight of base in hot benzene and allowing the solution to crystallise and also by dissolving the acid ( $1$  mol.) in dry ether, and adding an ethereal solution of the base ( $4$  mols.), but the same acid salt melting at  $146^\circ$  was obtained in both cases.

Attempts to obtain salts with diethyl- $\alpha$ - and - $\beta$ -naphthylamines led to the formation of gummy, uncrystallisable masses.

*D. Salts from 2:4:6-Trimethylbenzoic Acid.*

*Benzylamine 2:4:6-trimethylbenzoate* is obtained by separately dissolving equivalent amounts of the acid and base in light petroleum and mixing the solutions; it crystallises from benzene in small, feathery, colourless needles melting at  $165^\circ$ .

$0.3052$  gave  $0.1868$  trimethylbenzoic acid =  $61.2$ .

$\text{C}_{17}\text{H}_{21}\text{O}_2\text{N}$  requires  $60.5$  per cent.

Salts could not be obtained with this acid and any of the following

bases: dimethylmesidine, dimethyl- $\psi$ -cumidine, bromodimethyl-*m*-xylylidine, diethylaniline.

### E. Salts of the Three Toluic Acids.

*Benzylamine o-toluate*, obtained from light petroleum solutions of the acid and base, crystallises from benzene in small prisms melting at 146°. It dissolves readily in water, and to a moderate extent in light petroleum.

0.4716 gave 0.2668 *o*-toluic acid = 56.5.

$C_6H_4Me \cdot CO_2 \cdot NH_3 \cdot CH_2Ph$  requires 55.9 per cent.

$\psi$ -Cumidine hydrogen *o*-toluate,  $2(C_6H_4Me \cdot CO_2H) \cdot C_6H_2Me_3 \cdot NH_2$ , produced by mixing together ethereal or light petroleum solutions of the acid and base, crystallised from water in long, snow-white, silky needles, softening somewhat at 80° and melting at 82.5°. The same compound is obtained when an excess of the base is employed.

0.5 gave 0.3315 *o*-toluic acid (m. p. 105) = 66.3.

One mol. acid + 1 mol. base requires 50.18.

Two        „        „        „        „        66.8 per cent.

0.70 gram, when dissolved in sodium carbonate and extracted with ether, gave 0.236 gram of solid base = 33.7. The acid salt requires 33.2 per cent.

0.25 gram of the salt, when dissolved in ethyl alcohol, required 24.8 c.c. of *N*/20 baryta solution for complete neutralisation, using phenolphthalein as indicator. The acid salt requires 24.6 c.c.

Salts of *o*-toluic acid with dimethylaniline, dimethyl- $\psi$ -cumidine and dimethylmesidine could not be obtained.

Definite salts could not be obtained either from *m*-toluic acid and  $\psi$ -cumidine or dimethylaniline, or from *p*-toluic acid and the same bases.

### F. Salts from the Three Nitrobenzoic Acids.

$\psi$ -Cumidine *o*-Nitrobenzoate.—This salt was obtained in the form of silky needles when ethereal or benzene solutions of the constituents were mixed; when crystallised from water, it formed long, silky, prismatic needles melting at 133—134°.

0.4137 gave 0.2260 *o*-nitrobenzoic acid = 54.6.

$C_{16}H_{18}O_4N_2$  requires 55.3 per cent.

0.3 required 20.1 c.c. of *N*/20 baryta solution for neutralisation. The normal salt requires 19.9.

*Dimethyl-ψ-cumidine hydrogen o-nitrobenzoate*,  
 $2(\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}), \text{C}_6\text{H}_2\text{Me}_3\text{NMe}_2$ ,

obtained by mixing equal weights of the acid and base in benzene solution and crystallising from this solvent, forms small, colourless crystals melting at 124·5.

0·50 required 40·5 c.c. *N*/20 baryta solution. The acid salt requires 40·2 c.c.

*ψ-Cumidine m-nitrobenzoate* was obtained in the form of long, colourless, feathery needles melting at 129·5—130°, when the acid was mixed with twice its weight of *ψ*-cumidine and crystallised from benzene.

0·3 required 20·05 c.c. *N*/20 alkali. The normal salt requires 19·9 c.c. 0·5 requires 33·4 c.c. The normal salt requires 33·16.

The acid salt,  $2(\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}), \text{C}_6\text{H}_2\text{Me}_3 \cdot \text{NH}_2$ , was obtained when a mixture of the acid (2 mols.) and base (1 mol.) was dissolved in benzene and allowed to cool; it crystallises from water in pale yellowish needles melting at 144°.\*

0·40 required 34·3 c.c. of *N*/20 alkali. The acid salt requires 34·12 c.c.

A mixture of the two salts was obtained when equal weights of the acid and base were crystallised together from benzene or water.

The normal salt, when boiled with water, is partially transformed into the acid salt.

*Dimethyl-ψ-cumidine hydrogen m-nitrobenzoate*, obtained when molecular quantities of the acid and base are mixed in ethereal solutions, crystallises from benzene in small, colourless prisms melting at 119·5°, dissolves readily in alcohol, ether, or chloroform, but is only sparingly soluble in carbon disulphide or light petroleum, and crystallises from hot water in colourless, flat plates.

0·3566 gave 0·2362 *m*-nitrobenzoic acid = 66·2. The acid salt requires 67·2 per cent.

0·255 required 20·77 c.c. of *N*/20 alkali. The acid salt requires 20·52 c.c.

*ψ-Cumidine p-nitrobenzoate*, obtained by mixing ethereal solutions of the acid and base, separates from water in small, feathery crystals melting at 160°.

\* The salt mentioned previously (Trans., 1899, 75, 595) as melting at 140—141° must have been the acid salt, but the specimen actually analysed must have been the normal salt melting at 129·5—130°.

0.3246 gave 0.1872 *p*-nitrobenzoic acid = 57.6.

$\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2 \cdot \text{NH}_3 \cdot \text{C}_6\text{H}_2\text{Me}_3$  requires 55.3 per cent.

No definite salts could be obtained from dimethylaniline and the three nitrobenzoic acids.

#### G. Salts from the Three Bromobenzoic Acids.

$\psi$ -Cumidine *o*-bromobenzoate,  $\text{C}_6\text{H}_4\text{Br} \cdot \text{CO}_2 \cdot \text{NH}_3 \cdot \text{C}_6\text{H}_2\text{Me}_3$ , slowly separates in the form of fine needles from an ethereal solution of the acid and base; it dissolves readily in benzene, alcohol, or hot water, and crystallises from either light petroleum or hot water in colourless needles melting at 106—106.5°.

0.555 gave 0.3286 *o*-bromobenzoic acid = 59.2. The normal salt requires 59.8 per cent.

0.50 required 29.87 c.c. of *N*/20 alkali. The normal salt requires 29.76 c.c.

$\psi$ -Cumidine *m*-bromobenzoate crystallises from benzene in long, felted needles, melts at 98.5°, and is readily soluble in chloroform, alcohol, warm ether, or benzene.

0.50 required 29.7 c.c. of *N*/20 alkali. The normal salt requires 29.76 c.c.

No definite salts could be obtained from dimethylaniline and the three bromobenzoic acids, and an ethereal solution of  $\psi$ -cumidine and the *p*-bromo-acid slowly deposited crystals of the free acid melting at 251°.

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### XXX.—*Studies on the Electrolytic Oxidation of Phenols.* *Part I.*

By ARTHUR GEORGE PERKIN and FREDERICK MOLLWO PERKIN.

OF the numerous substances which can be obtained by the oxidation of pyrogallol and its derivations, one of the most interesting is purpurogallin, a compound possessing well-marked tinctorial properties. Originally prepared by Gerard from pyrogallol (*Ber.*, 1869, 2, 562) by the action of potassium permanganate and sulphuric acid, it has been

subsequently obtained from the same phenol by means of a most varied series of oxidising agents. In a recent communication, certain derivatives and decomposition products of this substance were described (Trans., 1903, 83, 192), from which it appears to have the formula  $C_{11}H_8O_5$ , and to be a derivative of naphthalene, as was first indicated by Nietzki and Steinmann (*Ber.*, 1887, 20, 1277). The formation of a naphthalene compound from pyrogallol, although very remarkable, is not unique, for a somewhat similar reaction is described by Zincke and Branke (*Annalen*, 1896, 293, 120), who prepared dibromo- $\beta$ -naphthaquinonecarboxylic acid by the action of nitric acid on bromoprotocatechuic acid. During the formation of these substances, it appears likely that a certain quantity of the phenol is converted by oxidation into an open chain compound, which then condenses with the phenyl residues.

Further work on the constitution of purpurogallin is in active progress, and it appeared possible that by a study of the electrolytic oxidation of pyrogallol some intermediate or secondary product might thus be prepared, and, moreover, it was anticipated also that if the colouring matter could be produced by this method, a considerably increased yield might be obtained. The following experiments indicate without doubt that by employing certain precautions the electrolytic method is the most suitable for the production of purpurogallin, for not only can the yield be thus augmented, but an almost chemically pure product is at once isolated. On the other hand, it has not as yet been found possible to prepare any intermediate compound which would be of service in elucidating the course of the reaction.

#### EXPERIMENTAL.

In selecting a suitable electrolyte, numerous substances were examined, and although purpurogallin was obtained in all instances, it was frequently contaminated with a brownish-black impurity, which rendered the method of little service. The employment of a 15 per cent. solution of sodium sulphate has been eventually adopted, and by this means a very pure bright orange-coloured product has been obtained. Solutions of sodium and ammonium acetates do not give satisfactory results, because when they are employed a somewhat poor yield of the impure alkali salt of purpurogallin is produced.

In the earlier experiments, the anode and cathode compartments were divided by means of a porous cell, but it subsequently appeared that better results could be obtained if the anode and cathode were not separated. Satisfactory results are obtained only when the anode is made of platinum and caused to rotate rapidly during the electrolysis. When a stationary anode is employed, the colouring matter is

apt to settle on the electrode, and is thus subjected to further oxidation. A rotating anode of lead, even when previously peroxidised, was very unsatisfactory, for in this case from 10 to 16 per cent. only of very impure purpurogallin could be obtained.\*

In carrying out the oxidation, 28 grams of pyrogallol dissolved in 500 c.c. of a 15 per cent. solution of sodium sulphate were placed in a rectangular glass jar, at two opposite corners of which were fixed two thin pieces of composition piping. On to each of the pipes a copper wire was soldered, and these were connected with each other by means of a screw connection and formed the cathode. The iridio-platinum anode had a surface of 1.5 square decimetres and was rotated rapidly by means of a water turbine or electromotor. During the electrolysis, the current density was kept at 2 amperes and the *E.M.F.* was 4.3—4.5 volts. To avoid a rise in temperature, the cell was surrounded with cold water. As soon as the current commenced to flow, the solution became yellow and a yellow precipitate gradually separated. When the electrolysis had continued for 8 hours, the product was left overnight, then collected, washed with water, and dried on a porous plate.

Satisfactory results were also obtained when, instead of rotating the anode, a rapid stream of air was blown through the mixture. In this case, the cathode consisted of a perforated leaden tube placed between two anodes of platinum foil, having a total surface of 4 square decimetres. The air, which was blown through the cathode during the operation, appears to help in the oxidation of the pyrogallol. Thus 445 grams of pyrogallol dissolved in a solution of 1 kilogram of sodium sulphate ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ) in six litres of water gave, after 35 hours' electrolysis, current density 9—10 amperes, *E.M.F.* 9.5—10.3 volts) 165 grams of purpurogallin or 37 per cent.

The average yield was 10.2 grams or 36.4 per cent., although on two occasions 13 grams (or 46.4 per cent.) were obtained. Nitrous acid yields only 25 per cent. of the crude product. That the substance thus obtained was practically pure is indicated by the analysis (A); the second estimation (B) was made on the product obtained with a lead anode, but this specimen was, however, first purified by crystallisation from acetic acid.

\* In the preparation of periodic acid by the electrolytic oxidation of iodic acid, with smooth platinum electrodes as anode, the yield is extremely small. But when peroxidised lead anodes are employed a very much better yield is obtained. The explanation being that the potential at which the oxygen is yielded up at the anode is higher with a lead peroxide anode than with one of polished platinum (*Ber.*, 1902, 35, 2652). In the case of pyrogallol, the probability is that when lead electrodes are used, the higher potential at which the oxygen is yielded causes the oxidation to be too vigorous.

Found (A) C = 60.03; H = 3.60. (B) C = 60.19; H = 3.60.

$C_{11}H_8O_5$  requires C = 60.00; H = 3.63 per cent.

The colouring matter was further characterised by conversion into the acetyl derivative, which was obtained in the form of yellow needles melting at 184—186°.

Found C = 58.87; H = 4.04.

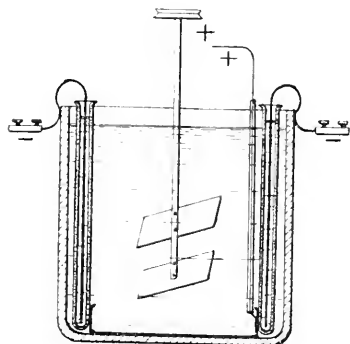
$C_{11}H_4O_5(C_2H_3O)_4$  requires C = 58.77; H = 4.12 per cent.

After one crystallisation from acetic acid, this product was found to be chemically pure.

Experiments were also tried with an alternating current, but although small quantities of purpurogallin were obtained, the method was not found satisfactory.

### *The Electrolytic Oxidation of Gallic Acid.*

It was previously shown that by the oxidation of gallic acid with potassium ferricyanide in the presence of sodium acetate a new substance, probably a purpurogallincarboxylic acid, is formed. As the yield by this method was extremely poor (3 per cent.) and the compound difficult to isolate, the electrolytic oxidation of gallic acid was studied in the hope that as in the case of pyrogallol a larger yield of a purer product would thus be obtained. Experiment showed that the purpurogallincarboxylic acid is rapidly obtained in this manner, and although the yield has up to the present been somewhat disappointing, it is evident that sufficient can be obtained by this process for a complete study of its constitution. After numerous trials, the following method was adopted.



It was found necessary to separate the anode and cathode compartments. A rectangular glass vessel was employed as before, on two sides of which were fitted two porous cells. These cells contained a piece of sheet lead, to which was soldered a stout copper wire. In order to keep the cells in position, the wire was bent over against the side of the glass jar as shown in the figure. The anodes consisted of a platinum stirrer and a stout wire bent up at each side against the bottom of the porous cells. To this wire was also welded a piece of platinum foil nearly large enough to cover the bottom of

the glass jar. The total active anode surface was about 1.75 square decimetres.

Various electrolytes were tried, but the only one which gave satisfactory results was a 15 per cent. solution of sodium or ammonium acetate acidified with acetic acid. In carrying out an electrolysis, 10—15 grams of gallic acid were dissolved in 600 c.c. of a 15 per cent. solution of ammonium or sodium acetate, 10 c.c. of glacial acetic acid were then added, and the mixture electrolysed. The cathode cells contained a similar solution. During the electrolysis, the cathode cells become too full and are apt to overflow; as the solution in these cells becomes strongly alkaline, it is necessary to remove a portion every now and then by means of a pipette in order to prevent it flowing over into the anode compartment. As soon as the current passes, the solution commences to turn brown and finally becomes almost black. After about 6 hours, the current is stopped, the electrodes and porous cells removed, the mixture left overnight, and then filtered, when a dark bronze-coloured product is obtained. This consists chiefly of the alkali salt of the acid in a somewhat crude condition. The yield varies very greatly, from 10 grams of gallic acid usually about 2 grams (or 20 per cent.) of the crude product are isolated, but we have obtained as much as 5 grams, or 50 per cent. The product of the reaction was purified as follows:

The substance ground into a thin cream with alcohol was diluted with some quantity of this solvent, a little hydrochloric acid added, and the mixture boiled for a minute or two; the solution obtained was then poured into ether, the ethereal extract washed with water, boiled with a little animal charcoal, filtered, and then evaporated to dryness. The orange-yellow, crystalline residue was collected, washed with water, then with ether, and dried.

Found C = 54.64; H = 3.52.

$C_{12}H_8O_7$  requires C = 54.54; H = 3.03 per cent.

It was found to be identical in all respects with the purpurogallin-carboxylic acid previously obtained from gallic acid by means of potassium ferricyanide.

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# XXXI.—*The Interdependence of the Physical and Chemical Criteria in the Analysis of Butter-fat.*

By THOMAS EDWARD THORPE, C.B., F.R.S.

IN July, 1901, a Departmental Committee was appointed, at the instance of the Board of Agriculture, to inquire and report as to what regulations, if any, might with advantage be made for determining what deficiency in any of the normal constituents of butter should raise a presumption that the butter was not genuine.

To assist the Committee in arriving at a conclusion on this matter, it became necessary to obtain at first hand the values of various analytical constants of specimens of butter of known origin, and produced from milk given under varying conditions. Observation has shown that the chemical nature of butter-fat is dependent to a certain extent on the climatic influences to which the cows are exposed, on the nature and amount of the food supplied, and on the breed, period of lactation, and idiosyncrasy of the individual cow. In order to give such weight as was practicable to the effect of these factors, the samples of butter were obtained from carefully selected districts, and often from cows set apart for the purpose of the inquiry; whilst particulars of the breed, diet, stabling, and period of lactation were supplied with the samples in nearly all cases. For example, to illustrate the effects of more rigorous climatic conditions than obtain in the United Kingdom generally, farms and dairies in Caithness, Sutherland, the Orkneys, Shetlands, and the Hebrides were laid under contribution; whilst a series of samples from Hollesley Bay, Suffolk, served to exemplify the influence of exposure of the cattle to the winds of the North Sea. From the arrangements made for the collection and transmission of the butter, it is believed that all the samples can be relied on as authentic. The analyses were made at the Government Laboratory.

Altogether about 430 samples were received; of these, for special reasons, 73 samples were only examined as regards water, salt, curd, and amount of fat, with which data we are not here concerned. The analytical figures obtained for the remainder, 357 in all, included, besides the foregoing particulars, determinations of the Reichert-Wollny number of the fat, its relative density and saponification value, and the Zeiss reading at 45°. In nearly all cases, the proportions of soluble and insoluble fatty acids were also determined, together with the mean molecular weight of the insoluble acids.

Details concerning the origin of the samples are published in the

Minutes of Evidence to the Report of the Committee (Cd. 1750, Appendix xxix, 505—588).

As relatively few systematic observations appear to have been made on authentic samples of British and Irish made butter having the representative character of those now dealt with, it may be useful to put on record a summary of the results obtained.

The object of the present communication is to indicate the general relations between the analytically-important chemical and physical constants of butter-fat as disclosed by a study of the average values of these constants determined on a number of samples sufficiently large to ensure with reasonable certainty a fairly close approximation to the true values.

Before attempting to make use of the observations with a view to general deductions, it is desirable to obtain some idea of the magnitude of the error to which the several determinations are liable. Taking first the Reichert-Wollny experiments, the results were obtained by working strictly under the conditions agreed upon by myself and a Committee representing the Council of the Society of Public Analysts, who in 1900 examined the matter in conjunction with analysts of the Government Laboratory in connection with the question of butter-fat in margarine (see Abstr., 1901, ii, 77). In a large number of duplicate experiments the mean difference obtained between two determinations of the Reichert-Wollny number on the same sample of butter-fat was 0.20. So far, therefore, as what may be called fortuitous errors are concerned, the average values may be taken as known to within about  $\pm 0.1$  unit where the value is obtained from a fairly large number of samples, and probably to within  $\pm 0.2$  unit where the number is relatively small.

The relative densities of the fats were generally taken in a pycnometer of bottle form, adjusted to contain 50 grams of water at  $37.8^{\circ}$ . Duplicate weighings of the same fat with such a pycnometer rarely differ by more than 0.005 gram, corresponding with one unit in the fourth decimal place when expressed as specific gravity. In a few cases a bottle of only half the above capacity was used; the error here might be twice as great as with the larger pycnometer, or two units in the fourth decimal place. Consequently the average values may, as regards the variable errors of experiment, be looked upon as accurate to within  $\pm 0.0001$ .

A small constant error might conceivably arise thus: after the fat in the bottle has been brought to the desired temperature of  $37.8^{\circ}$  a little time is required to complete the filling and to insert the stopper. During this time, the temperature is falling, and the effect of this would be to slightly increase the weight of fat which the bottle would contain. The same tendency would, however, be found during

the adjustment of the instrument with water, and the actual error would therefore be only that arising from the difference of these effects. It would be small, and sensibly constant.

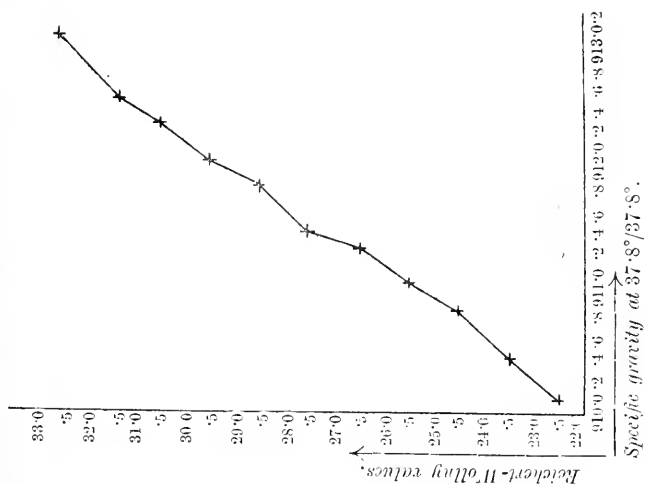
The average difference shown by duplicate determinations of the saponification value of butter-fat, deduced from a large number of experiments made by several operators, was found to be 0.065, expressed as percentage of potassium hydroxide. This corresponds to about 0.7 of a unit when calculated into "saponification-equivalents." Substantially the same difference was found in the case of the molecular weight determinations. The values may, therefore, be regarded as subject to an experimental error of about  $\pm 0.4$  of a unit. In all cases the acid and alkali used were carefully standardised, and it is not thought that any appreciable error is to be attributed to this part of the experimental work.

As regards the refractometer indications, it may be noted that there are two or three possible sources of inaccuracy in using the Zeiss butyro-refractometer. (1) Since the instrument is graduated into divisions representing whole units, the fractions of a unit have to be estimated by the eye. (2) The line of shadow is often not very sharply defined where it cuts the scale of the instrument. (3) The temperature may fluctuate slightly during the course of the experiment. Probably a single observation might be liable to a maximum error of  $\pm 0.4$  unit, and the mean of a number of experiments such as are used in the curves given below may be relied upon as accurate within about  $\pm 0.2$  of a unit.

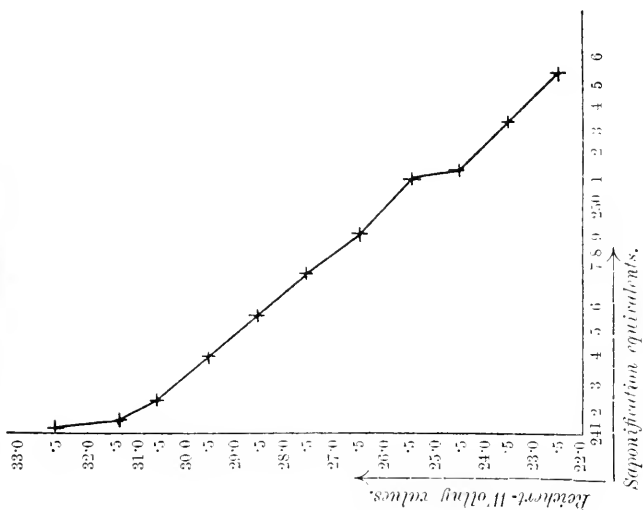
For the soluble and insoluble acids, the method adopted was substantially the modification of Hehner's process recommended by the American Association of Official Agricultural Chemists. The saponification of the fat, however, was effected in silver flasks instead of in glass. For the soluble acids, the mean difference between duplicate analyses in a large number of cases was found to be 0.12 per cent., and for the insoluble acids 0.15 per cent. So far as manipulative error is concerned the average values given in the table may therefore be taken as accurate to within about  $\pm 0.06$  and  $\pm 0.08$  per cent. in the two cases respectively.

The averages of the analytical data from which the curves given below are constructed are given on p. 254. In obtaining these figures—taking, for example, the first line—all the Reichert-Wollny values lying between 22.00 and 22.99 have been taken from the experimental results and averaged, giving the number 22.5. The corresponding values of the specific gravity, saponification-equivalent, and Zeiss number were also abstracted and averaged, giving the figures shown in the table. For the next line, the Reichert-Wollny values lying between 23.0 and 23.99 were taken; and so on for the others.

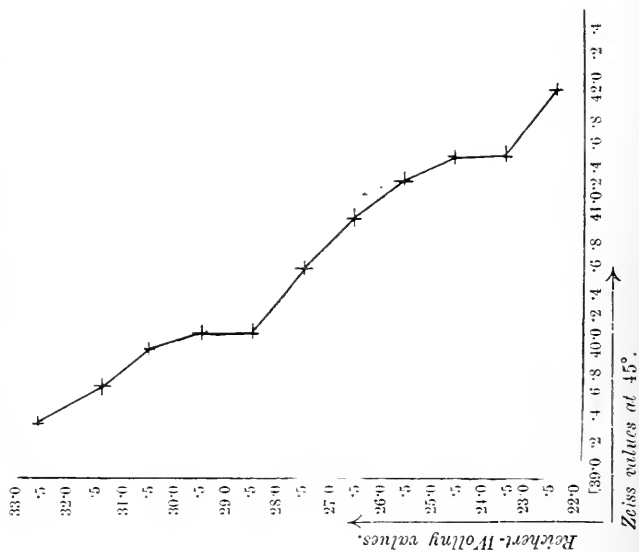
No. 1.—Variation of specific gravity with Reichert-Wollny number.



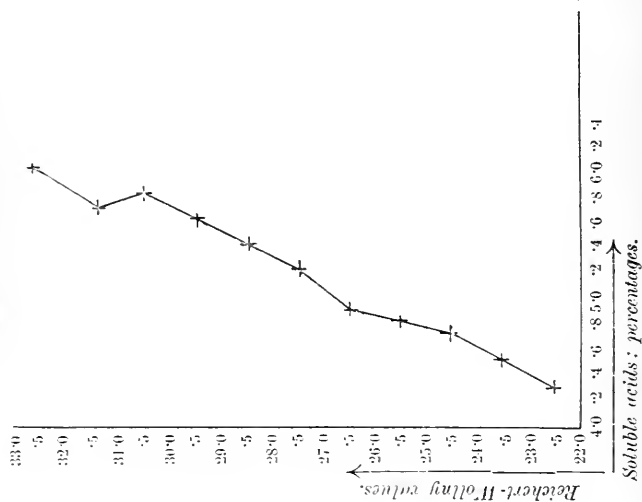
No. 2.—Variation of saponification equivalent with Reichert-Wollny number.



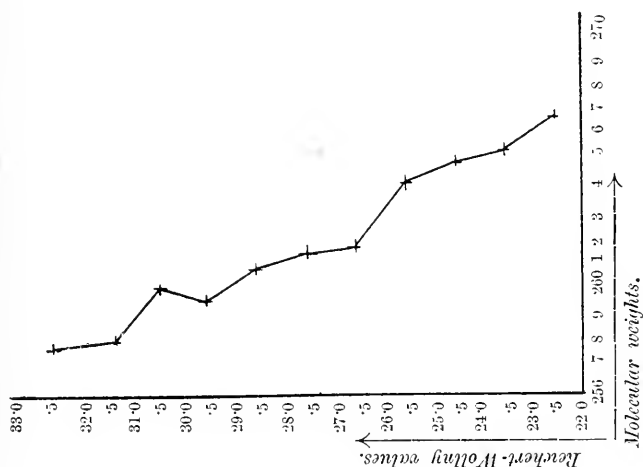
No. 3.—Variation of Zeiss value with Reichert-Wollny number.



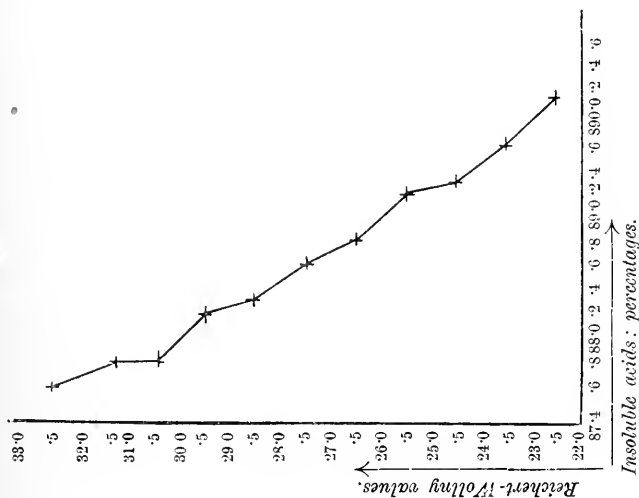
No. 4.—Variation of soluble acids with Reichert-Wollny number.



No. 6.—Variation of the mean molecular weight of the insoluble acids with the Reichert-Wollny number.



No. 5.—Variation of insoluble acids with Reichert-Wollny number.



No. of samples.	Reichert-Wollny number.	Specific gravity at $37.8^{\circ}$ $37.8^{\circ}$	Saponification equivalent.	Zeiss number. $45^{\circ}$ .	Soluble acids.* Per cent. on fat.	In-soluble acids. Per cent. on fat.	Mean molecular weight of insoluble acids.
7	22.5	0.9101	255.4	42.0	4.3	90.1	266.9
17	23.5	0.9104	253.4	41.5	4.5	89.7	265.5
15	24.5	0.9108	251.3	41.5	4.7	89.4	265.0
27	25.5	0.9110	251.1	41.3	4.8	89.3	264.2
37	26.5	0.9113	248.9	41.0	4.9	88.9	261.9
51	27.5	0.9114	247.4	40.6	5.2	88.7	261.7
78	28.8	0.9118	245.7	40.1	5.4	88.4	260.9
56	29.5	0.9120	244.0	40.1	5.6	88.3	259.6
41	30.5	0.9123	242.4	39.9	5.8	87.9	260.1
18	31.3	0.9125	241.5	39.7	5.7	87.9	258.0
10	32.6	0.9130	241.2	39.4	6.0	87.7	257.8
357							

\* Calculated as butyric acid.

Two or three samples, the data for which would fall beyond the extremities of the curves given, have been omitted on account of the number of observations being insufficient to afford trustworthy average values.

As regards the probable errors of the observations, it may be remarked that any constant error pertaining to a process will not, when the results are presented in the form of curves, affect the shape of the curve; it will only alter its position relative to the axes. Such errors are those which, for example, might arise from the thermometer of a Zeiss instrument having altered since the refractometer was standardised, or from the retention in the distilling-flask of a small constant quantity of volatile acids in determining the Reichert-Wollny figure. On the other hand, errors of manipulation and observation, the incidence of which is sometimes on one side of the truth, sometimes on the other, will, in accordance with statistical principles, be largely nullified by taking the averages of a sufficiently large number of experiments. Curves plotted, therefore, from the mean results of many observations should show with some degree of accuracy the general tendency of the relations between the several constants, and illustrate their interdependence.

A few comments may be made on these curves. It will be seen that, in a general sense, the relative density of butter-fat increases as the Reichert-Wollny number is augmented. This would, of course, follow from the well-known fact that the glycerides of low molecular weight have a greater density than the glycerides of the higher fatty acids which occur in butter. Very approximately, the increase is

directly proportional to the increase in the Reichert-Wollny values, as is shown by the curve approaching more or less closely to a straight line.

Speaking broadly, the variations of the saponification numbers are in inverse relation to those of the Reichert-Wollny values and the relative densities; but they show, as from the nature of the case might be expected, some notable departures from proportionality in the amount of variation. The aberrations are most marked towards the extremities of the curve. Here the observations are fewer in number than those from which the middle of the curve is constructed, but it is not likely that any presumable experimental error would account for the variations shown. When it is considered that the saponification-equivalents of the glycerides of the volatile fatty acids range from 100·6 for tributyrin to 212·6 for trilaurin,\* whilst those of the glycerides of the non-volatile acids vary between 240·7 for trimyristin and 296·6 for tristearin, it will be obvious that even small variations in the relative proportions of the glycerides may affect rather considerably the mean saponification-equivalent of the whole fat.

Somewhat similar remarks apply to the Zeiss numbers. These generally decrease in magnitude as the Reichert-Wollny values increase, but the rate of diminution is not regular, and this points, like the variations of the saponification-equivalent, to changes in the proportions of the individual acids which, in butter-fat, constitute the "volatile" and "non-volatile" groups respectively.

The curve showing the mean molecular weights of the insoluble acids is of some interest, from the physiological problem which it suggests. From it we infer that, as the acids of low molecular weight increase in amount, the mean molecular weight of the remaining acids decreases, and, broadly speaking, decreases proportionally. This may indicate one of several things. Remembering that the molecular weights of the insoluble acids which are believed to occur in butter are as follows: lauric (200),† myristic (228), palmitic (256), oleic (282), stearic (284),‡ and that the mean molecular weights dealt with in the table decrease from 266·9 to 257·8, it will be seen that this decrease may be due to one of the following causes. In the first place, it may be due to a diminished proportion of oleic acid. Or, the oleic acid remaining the same, the decreased molecular weight may be due to a displacement of palmitic acid by myristic and lauric acids, one or both; or, possibly, of myristic by lauric acid. Finally, if the oleic acid increases, this can

\* Or to 184·7 for tricaprin.

† Lauric acid is said to be slightly soluble in water and appreciably volatile when distilled with steam.

‡ Apparently stearic acid exists in butter to a small extent only. If this is so, it may be neglected in the present connection.

only be compensated for, and the decreased mean molecular weight explained, by an increase in the amount of lauric acid, with a simultaneous decrease in the myristic and palmitic acids. The physiological question which presents itself is whether the metabolic changes which, in the bovine organism, result in the production of an increased proportion of the lower saturated fatty acids, bring about this production at the expense of the oleic acid.

Judging from the values obtained for the iodine-absorption of a number of the specimens, it would seem that, speaking generally, a low proportion of volatile acids in butter-fat is associated with a high percentage of oleic acid, and *vice versa*. The figures are as follows :

	Reichert- Wollny number.	Iodine value.	} = Oleic acid.		Insoluble acids.	Mean molecular weight of insoluble acids.
(1) Average of 20 samples	24.2	40.0	44.4	per cent.	89.6 per cent.	264.6
(2) 30 ,,	30.8	32.4	36.0	,,	88.1 ,,	259.8

In the first series, the oleic acid constitutes 49.6 per cent. of the insoluble acids; in the second series, 40.9 per cent. This decrease in the proportion of oleic acid would diminish the mean molecular weight of the insoluble acids from 264.6 to 261.5. The actual figure obtained for the molecular weight in the second series being 259.8, it would appear that the decrease is largely, but not entirely, brought about by the diminution in the proportion of oleic acid.

Since the whole of the decrease is not accounted for by the oleic acid, it follows that the mean molecular weight of the insoluble saturated acids is lower in the second series than in the first. In fact the values, calculated from the foregoing table, are 247.4 and 244.4 respectively.

It should be mentioned that the iodine-values were determined after the fats had been kept some time, and they are not given as representing precisely the values for the fresh fat. It is well known that the oxidation changes which may take place during the keeping of butter-fat tend to affect the iodine number. Nevertheless, since the two groups cover practically the same dates and were kept side by side until examined, it may be assumed that, on the whole, they would be about equally affected, and the relative values of the averages would remain substantially unchanged.

THE GOVERNMENT LABORATORY,  
LONDON.

# XXXII.—*A Simple Thermostat for Use in Connection with the Refractometric Examination of Oils and Fats.*

By THOMAS EDWARD THORPE, C.B., F.R.S.

IN the Government Laboratory, as in other laboratories where large numbers of commercial oils and fats, and especially butter, are required to be examined, the Zeiss butyro-refractometer has proved to be of great service. As is well known, it is generally necessary in using the instrument to allow a current of water of constant temperature to flow through the apparatus for some little time before making the readings, and it was with the view of rapidly and easily obtaining this current that the little contrivance seen in the accompanying figure was devised in substitution for the special heating arrangement supplied with the instrument, which was found to be somewhat cumbrous and uncertain in action.

The temperature employed in the refractometric examination of butter-fat is  $45^{\circ}$ , and it must be understood, therefore, that the details of the arrangement as described have been adjusted in order that the circulating water shall give this temperature as indicated by the thermometer attached to the refractometer. It is, however, possible, by a slight rearrangement of the details, to obtain a considerable range of constant temperatures.

The principle of the thermostat and the method of working it will be obvious from the figure. The apparatus consists essentially of a vessel for generating steam or other appropriate vapour, containing a coil through which the current of water flows and is heated before it passes through the refractometer or other instrument, the position of which is shown in the drawing at Z, by which the observations at a given constant temperature are to be made.

In the figure (p. 258), A represents a metallic cylindrical vessel 5 cm. in diameter and 5 cm. deep, containing approximately 100 c.c. of water, &c., for generating steam, &c.

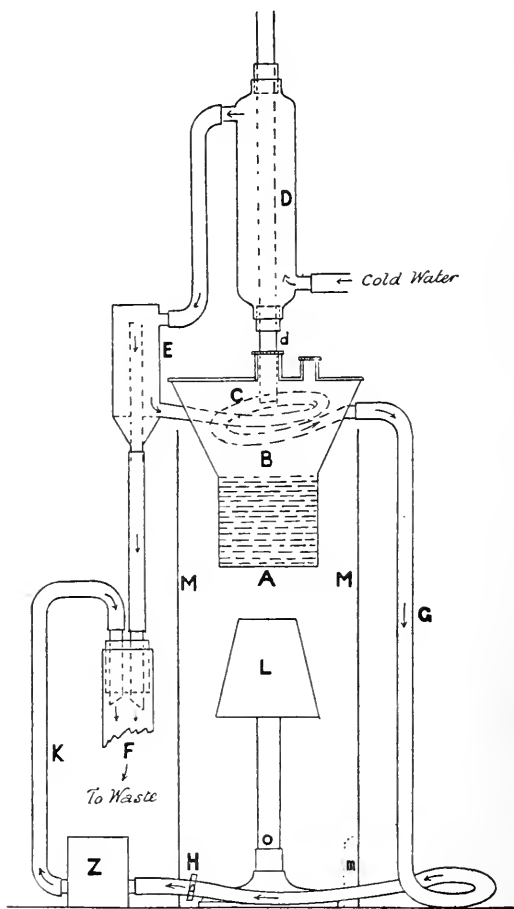
B, a conical steam-chamber, in which the coil, C, is suspended and heated by the steam from A. The diameter of cover is 10 cm.

C, a coil of copper or "compo," tubing, from 25 cm. to 30 cm. long, and having an internal diameter of about 3 mm. The current of water passing through the coil is heated before entering the instrument, Z.

D, a reflex condenser, preferably of glass, held in position by a tubulure, *d*, provided with a sliding or screw cap to prevent loss of the liquid in A.

E, an arrangement for maintaining a constant head of water at the

point of entrance to the coil, so as to reduce variations in the temperature of Z, due to fluctuations in the pressure of the current of water. It consists of an outer metal tube, through which a narrow central tube rises, and serves as an overflow when the water in the outer tube has reached the level of its upper orifice.



F, a stout glass tube, acting as a gauge or "tell-tale," to indicate whether or not the overflow and the current of water through the instrument, Z, are running properly.

G, a thick-walled caoutchouc tubing (for example, pressure-tubing), to minimise loss of heat during the passage of water from the coil to the instrument, Z.

H, a screw clamp, for regulating the rate of flow of water through the coil and through the instrument, Z. The final adjustment of the desired temperature may be made by means of the screw clamp.

K, a caoutchouc tubing, carrying away waste water from the instrument, Z, and terminating in the gauge, F, where the rate of the current can be observed.

L, Bunsen burner with cone.

M, a metallic cylinder for protecting Bunsen flame from draughts, and to reduce loss of heat due to radiation from walls of the steam generator. At the foot is a semicircular opening, *m*, for the admission of the gas tube.

This little apparatus has been in use for some years in the Government Laboratory, and has been found to answer its purpose sufficiently well. Only a few minutes are needed to bring it into action, and, under ordinary working conditions, it is readily possible to secure a steady current of water, not varying more than  $0.1^{\circ}$  or so in temperature throughout the day.

THE GOVERNMENT LABORATORY,  
LONDON.

### XXXIII.—*The Action of Nitrogen Sulphide on Organic Substances. Part I.*

By FRANCIS ERNEST FRANCIS and OLIVER CHARLES MINTY DAVIS.

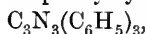
AN investigation of the action of nitrogen sulphide on organic substances has been undertaken in the hope that it may throw some light on the constitution of this substance.

Nitrogen sulphide is formed together with other products when ammonia acts on a solution of sulphur dichloride in carbon disulphide or benzene. According to the investigations of Fordos and Gélis (*Compt. rend.*, 1850, 31, 702), this substance has the empirical formula NS. The molecular weight, which was first given by Schenck as  $N_4S_4$ , was determined by the cryoscopic method in naphthalene, and this was confirmed by Muthmann (*Ber.*, 1896, 29, 340), who obtained the same result with the ebullioscopic method in carbon disulphide. By employing the latter method, with benzene as solvent, we have also found the same molecular complexity.

The sulphide is best prepared by passing ammonia into a 10—15 per cent. solution of sulphur dichloride in benzene. When the ordinary chloride is employed, the yield is much smaller. A rapid

current of the dry gas is passed into the solution until red fumes appear, the flask in which the operation is being conducted is then cooled, and on maintaining the current for a short time the reaction is completed. After filtering off the ammonium chloride formed, the solution, on evaporation, deposits long, orange-red prisms of nitrogen sulphide. This is a beautifully crystalline substance, and may be readily purified by recrystallisation from either boiling benzene, toluene, or carbon disulphide; our specimens always showed a perfectly constant decomposition point at  $185^{\circ}$ , although Muthmann gives  $178^{\circ}$ , and earlier determinations were even lower, these results being probably owing to contamination with free sulphur. The properties of nitrogen sulphide have been fully described, but it may be of interest to state that Prof. Muthmann informed us that it was unwise to keep more than a few grams of the substance in one vessel, since it is apt to explode spontaneously with considerable violence. Although dealing with moderately large quantities, we have never observed this change, and are inclined to believe that the sulphide is rather more stable than is usually supposed.

The first group of organic substances investigated were the aromatic aldehydes. With benzaldehyde, a violent reaction takes place near the boiling point of this liquid; sulphur dioxide and water are evolved, and considerable amounts of triphenylcyanidine (cyaphenin),



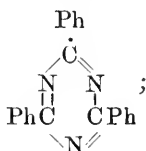
are formed. The reaction proceeds more slowly at lower temperatures, and at  $100^{\circ}$  was complete in about 30 hours. In each case, the main product is cyaphenin, and a much smaller quantity of a less fusible, crystalline substance, which was only isolated with difficulty. This product appears to be  $\alpha\beta\mu$ -triphenylglyoxaline or lophin,  $\text{C}_3\text{N}_2\text{H}(\text{C}_6\text{H}_5)_3$ ; it is probably formed by the reduction of cyaphenin by sulphur dioxide; this view of its formation is strengthened by the fact that small quantities of ammonium sulphate were detected among the products of the reaction. This interesting reaction does not seem to be dependent on the intermediate formation of benzonitrile, since nitrogen sulphide does not yield cyaphenin when treated with this substance. Benzylideneaniline, in a similar way, yields cyaphenin, and we are at present investigating the other products of this reaction. With *p*-tolaldehyde and nitrogen sulphide, the action is very similar, and the corresponding tritolycyanidine is easily obtained.

G. Glock (*Ber.*, 1888, 21, 2652) described the preparation of a polymerised toluonitrile, which he considered was probably "kyantolin," and there is no doubt that the substance he obtained is identical with our preparation, which, judging from the method of its formation, is very probably tritolycyanidine,  $\text{C}_3\text{N}_3(\text{C}_6\text{H}_4\cdot\text{CH}_3)_3$ .

With anisaldehyde and nitrogen sulphide, the action proceeds rather

more rapidly at  $100^{\circ}$  than in previous cases, and the main product is a white, crystalline powder which is still under investigation. We only found it possible to isolate very small quantities of what appeared to be tri-*p*-methoxyphenylcyanidine,  $C_3N_3(C_6H_4 \cdot O \cdot CH_3)_3$ . Like cyanophenol, this substance, although only slightly soluble in boiling alcohol, is readily recrystallised from hot benzene; it dissolves in concentrated sulphuric acid to a deep yellow solution, and is precipitated unchanged on the addition of water. Similarly, it has been found by one of us that salicylonitrile, on heating, readily polymerises into a yellow, crystalline compound with a high melting point, this product being also soluble without decomposition in concentrated sulphuric acid giving a yellow solution. From its great stability, it is not decomposed at  $350^{\circ}$ , and from the fact that its molecular weight was found to be approximately three times that of salicylonitrile, it appears probable that this substance is tri-*o*-hydroxyphenylcyanidine,  $C_3N_3(C_6H_4 \cdot OH)_3$ . Want of material prevented us from obtaining the corresponding tri-*p*-hydroxyphenylcyanidine from the foregoing trimethyl ether and comparing its reactions with those of the *o*-derivative.

The constitution of these cyanidines or 1:3:5-triazine compounds may in all probability be represented by the formula



they are very stable substances having high melting points, and they are not decomposed by aqueous or alcoholic potassium hydroxide. The cyanidine ring is broken by reducing agents, as when the triphenyl derivative yields lophin,  $\begin{array}{c} C_6H_5 \cdot C \cdot NH \\ | \\ C_6H_5 \cdot C - N \end{array} \gg C \cdot C_6H_5$ . The complete decomposition into ammonia and benzoic acid can, however, only be effected by more powerful reducing agents, such as hydriodic acid at  $220^{\circ}$ .

We are at present pursuing the investigation of the interaction of nitrogen sulphide and aldehydes, and propose trying similar reactions with other groups of organic substances.

#### EXPERIMENTAL.

##### 1. Action of Nitrogen Sulphide on Benzaldehyde.

Two grams of nitrogen sulphide were dissolved in a small quantity of benzene and treated with 10 grams of benzaldehyde; no reaction took place on boiling for 8 hours. On distilling off the benzene and

heating with a free flame, the reaction became violent near the boiling point of the aldehyde, sulphur dioxide, water, and the excess of aldehyde distilled off, and the solid residue, after repeated crystallisation from benzene, gave about 1.3 grams of triphenylcyanidine.

The following results were obtained on analysis:

C = 81.52; H = 5.18; N = 13.61.

$C_3N_3(C_6H_5)_3$  requires C = 81.55; H = 4.85; N = 13.59 per cent.

The melting point was  $230^\circ$ , the numbers given for triphenylcyanidine by different authors being between  $231^\circ$  and  $233^\circ$ .

An attempt was made to follow quantitatively the course of the reaction, but without any very definite result. One gram of nitrogen sulphide was treated with a large excess of benzaldehyde, the operation being carried out in absence of air, and the sulphur dioxide liberated passed into a standard iodine solution. It was found that, approximately, 0.2 gram of sulphur was liberated as sulphur dioxide, and, after distilling off the unchanged aldehyde, nearly 0.12 gram was obtained from various crystallisations, the amount unaccounted for being 0.37 gram. The experiment could only, of course, be regarded as an approximation, but in attempting to account for the loss in sulphur, we were led to detect, among the residues, ammonium sulphate (in another experiment, carried out under similar conditions, this amounted to nearly 1 gram, which was equivalent to 0.24 gram of sulphur) and a substance much more soluble in absolute alcohol, and less so in benzene than triphenylcyanidine. The isolation of the latter substance in the pure state was extremely difficult, and, judging from the analysis given later, the compound we eventually obtained was not quite pure. The reaction between the aldehyde and nitrogen sulphide was then carried out on a larger scale, and the excess of aldehyde removed by distillation in steam; the aqueous solution in the distilling flask contained ammonium sulphate and a very small quantity of a substance containing nitrogen, but not sulphur; this was extracted by means of ether, recrystallised from benzene, and found to melt at  $128^\circ$ . The amount obtained was insufficient for an analysis. The residual solid, insoluble in water, was dried and treated several times with boiling alcohol; from the filtrate, small quantities of triphenylcyanidine crystallised on cooling, and on adding water it was found that the substance which separated had a much higher melting point. On repeating this process many times, a white, feathery, crystalline mass was eventually obtained, only slightly soluble in benzene, but much more so in alcohol, from which it crystallises in characteristic tufts. From its appearance, we thought it might be lophin, although its melting point was  $265$ — $267^\circ$ , whereas that substance is stated to melt at  $275^\circ$ . The following data were obtained on analysis:

C = 85.63 ; H = 5.66 ; N = 9.87.

(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>C<sub>3</sub>N<sub>2</sub>H requires C = 85.13 ; H = 5.40 ; N = 9.46 per cent.

Laurent and Brunner (*Annalen*, 1869, 151, 135) state that lophin gives a hydrochloride melting at 155°, which is soluble in alcohol but insoluble in water. In order to confirm our view that we were actually dealing with this substance, the small amount at our disposal was converted into the hydrochloride, which decomposed at 157—159°, and was soluble in alcohol but insoluble in water. In all probability then, the substance was impure lophin, formed, possibly, by the reduction of triphenylecyanidine by sulphur dioxide, this view of its formation being strengthened by the presence of ammonium sulphate in the products of the reaction. We were unable to obtain a better yield of this substance, and as many experiments gave only 0.7 gram of this product, its further investigation was consequently abandoned. The reaction between the aldehyde and nitrogen sulphide was then carried out in an inert atmosphere at 100°, and although the velocity of the reaction was thereby greatly reduced—the time required for 5 grams of nitrogen sulphide to react being about 30 hours—yet the products were very similar. The yield of triphenylecyanidine was slightly increased, the amount of free sulphur was not quite so large, and the lophin was formed in about the same proportion as in previous cases. When benzylideneaniline was employed in place of benzaldehyde, the reaction takes place much less energetically, and the products contained triphenylecyanidine and a large amount of an oil which we are at present investigating.

## 2. Action of Nitrogen Sulphide on *p*-Tolualdehyde.

On warming together *p*-tolualdehyde and nitrogen sulphide, a reaction takes place very similar to that described with benzaldehyde; the solution darkens on heating, sulphur dioxide is slowly evolved, and a crystalline substance separates, which, after washing with ether and recrystallising from boiling benzene, melts sharply at 278°; it is slightly soluble in boiling alcohol and crystallises from hot benzene in long needles. The following results were obtained on analysis:

C = 82.32 ; H = 6.20.

C<sub>3</sub>N<sub>3</sub>(C<sub>6</sub>H<sub>4</sub>·CH<sub>3</sub>)<sub>3</sub> requires C = 82.05 ; H = 5.98 per cent.

This substance appears to be identical with a polymeride of toluonitrile, termed by Gustav Glock "kyantolin" and described as crystallising in long needles melting above 260°.

3. *Action of Nitrogen Sulphide on Anisaldehyde.*

Five grams of nitrogen sulphide were heated for 20 hours with 12 grams of anisaldehyde in an inert atmosphere. The solid mass obtained at the end of that time was extracted with boiling alcohol to remove any unchanged aldehyde, and then extracted with boiling benzene. The insoluble matter constituted by far the larger bulk (about 5.6 grams); it was a white, crystalline powder, partially soluble in water, and at present it is still under investigation. The soluble matter consisted chiefly of sulphur, together with a very small quantity of a substance crystallising from benzene in white leaflets, and best separated from the sulphur by solution in acetone or concentrated sulphuric acid. This compound melts sharply at  $217^{\circ}$ , and is but slightly soluble in alcohol. On analysis, it gave the following result:  $N = 10.70$ .  $C_3N_3(C_6H_4 \cdot O \cdot CH_3)_3$  requires  $N = 10.52$  per cent.

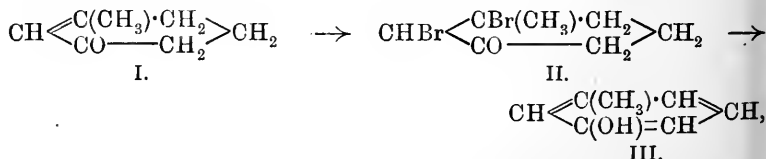
It appears to be tri-*p*-methoxycyanidine, which is soluble in concentrated sulphuric acid forming a deep yellow solution and is precipitated unchanged on the addition of water. As previously mentioned, tri-*o*-hydroxycyanidine is a yellow, crystalline substance also soluble in sulphuric acid to a yellow solution.

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# XXXIV.—*Aromatic Compounds obtained from the Hydroaromatic Series. Part I. The Action of Bromine on 3:5-Dichloro-1:1-dimethyl- $\Delta^{2:4}$ -dihydrobenzene.*

By ARTHUR WILLIAM CROSSLEY.

MANY instances have been recorded of the conversion of hydroaromatic into aromatic substances under the influence of such reagents as bromine or nitric acid. For example, 1-keto-3-methyl- $\Delta^2$ -tetrahydrobenzene (I) readily absorbs two atoms of bromine to form an unstable product (II) which loses two molecules of hydrogen bromide yielding *m*-cresol (III) (Knoevenagel, *Ber.*, 1893, 26, 1951):



and with nitric acid, 1:3-dimethyldihydrobenzene gives mono-, di-, and tri-nitroxylenes (Wallach, *Annalen*, 1890, 258, 319).\*

This direct conversion of hydroaromatic into aromatic substances has often been of fundamental importance as a method for determining the constitution of a hydroaromatic compound when, by its transformation into an aromatic derivative of known constitution, the relative positions of its substituting groups have been ascertained. But the method is not always valid, for instances are known in which an alkyl group wanders during the conversion (Baeyer and Villiger, *Ber.*, 1898, 31, 2068).

Recently it has been shown that 3:5-dichloro- $\Delta^{2:4}$ -dihydrobenzene under the influence of excess of phosphorus pentachloride or bromine is converted into *m*-dichlorobenzene (Trans., 1903, 83, 495) and that 3:5-dichloro-1:1-dimethyl- $\Delta^{2:4}$ -dihydrobenzene, when acted on with excess of phosphorus pentachloride, is converted into 3:5-dichloro-*o*-xylene (Trans., 1902, 81, 1536):



also when phosphorus pentabromide acts on dimethyldihydroresorcin brominated *o*-xlenols are produced (Trans., 1903, 83, 116).

In the two latter cases, the reaction is complicated by the fact that, as the original substance contains the *gem*-dimethyl group, the migration of one of these methyl groups becomes an essential step in the production of the aromatic compound.

As a quantity of 3:5-dichloro-*o*-xylene was wanted for another research, and as the action of bromine on dichlorodihydrobenzene had resulted in the formation of *m*-dichlorobenzene as the main, if not the sole product, it was thought advisable to try the action of bromine on 3:5-dichloro-1:1-dimethyl- $\Delta^{2:4}$ -dihydrobenzene (Trans., 1902, 81, 827). From the desired point of view, the reaction is disappointing, inasmuch as only a very small quantity of 3:5-dichloro-*o*-xylene is formed, but it has afforded an interesting example of the passage from hydroaromatic to aromatic substances, and as it is, on account of the symmetry of the molecule, one of the simplest cases in which the wandering of an alkyl group can take place, it has been worked out, so as to gain an insight into the course of such reactions. Moreover, as the dimethyldihydroresorcin, which forms the starting point of the investigation, is readily obtained from aliphatic substances (ethyl

\* The following are references to a number of typical examples of reactions involving the conversion of hydroaromatic into aromatic substances: Schweitzer, *J. pr. Chem.*, 1841, 24, 257; Wallach, *Annalen*, 1877, 187, 159; Baeyer, *Ber.*, 1892, 25, 1037; Knoevenagel, *Ber.*, 1894, 27, 2347; Einhorn and Willstätter, *Annalen*, 1894, 280, 88; Zelinsky, *Ber.*, 1895, 28, 782, and 1901, 34, 2803; Baeyer and Villiger, *Ber.*, 1898, 31, 1401, 2067; Klages, *Ber.*, 1899, 32, 1516; Crossley and Le Sueur, Trans., 1902, 81, 831, 1533, and 1903, 83, 116; Crossley and Haas, Trans., 1903, 83, 495.

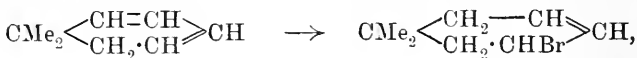
malonate and mesityl oxide, Trans., 1899, '75, 772), the subject becomes of interest as helping to connect together the aliphatic and aromatic series.

The main products of an aromatic nature obtained when bromine acts on dichlorodimethyldihydrobenzene are the two theoretically possible dichlorobromo-*o*-xylenes containing the chlorine atoms in the 3:5-position, and no substance has been encountered in which an alkyl group has wandered into any but an ortho-position.

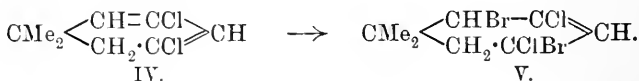
The reaction is largely influenced by the condition of experiment, entirely different results being obtained according as to whether one or two molecules of bromine are employed.

When dichlorodimethyldihydrobenzene, dissolved in a small amount of chloroform, is treated with bromine, so long as this reagent is used up a quantity is absorbed corresponding almost exactly with two molecular proportions, and during the later stages of the reaction volumes of hydrogen bromide are evolved. The product consists mainly of a viscid, syrupy liquid, which, on distillation, or preferably when left in a vacuum over potassium hydroxide, gives 3:5-dichloro-4-bromo-*o*-xylene (see page 275); and to a smaller extent of a beautifully crystalline solid having the formula  $C_8H_9Cl_2Br_3$ . This substance is evidently a *dichlorotribromodimethyltetrahydrobenzene*, but the exact position of the halogen atoms cannot be readily ascertained.

It has been shown (Trans., 1902, 81, 823) that when 1:1-dimethyl- $\Delta^{2:4}$ -dihydrobenzene is treated with bromine or hydrogen bromide, only one molecule of either reagent is absorbed, in the latter case giving rise to 5-bromo-1:1-dimethyl- $\Delta^3$ -tetrahydrobenzene,



and presumably, therefore, the first action of bromine on dichlorodimethyldihydrobenzene would consist in the direct addition of two atoms of bromine in a similar way, giving rise to a *dichlorodibromodimethyltetrahydrobenzene* (V), having the following constitution:

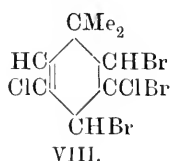
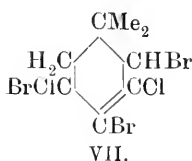
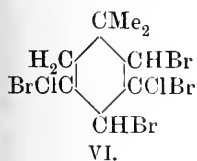


Notwithstanding the fact that the product contains a double linking, the net result of the second phase of the reaction is the replacement of hydrogen by bromine in this compound.

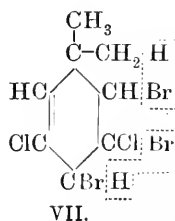
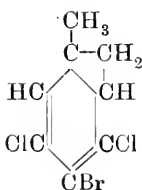
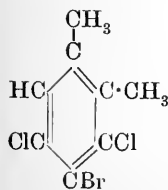
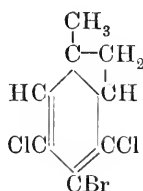
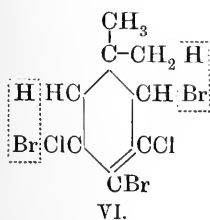
It is a well-known fact that substances containing two double linkings in the position indicated in formula IV,  $\cdot C:C:C:C \cdot$ , do add on bromine at the terminal carbon atoms with the formation of a new double bond between the central carbon atoms,  $\cdot C:C:C:C \cdot$ , and that this new bond often does not perform the ordinarily accepted func-

tions of an unsaturated linking by taking up a further molecule of bromine to give a saturated substance. Such appears to be the case with the compound under discussion, for in order to obtain a derivative having the formula  $C_8H_9Cl_2Br_3$  from the unsaturated compound (V), one hydrogen must be replaced by bromine.

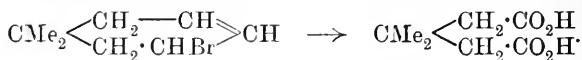
In discussing the position of this bromine atom, it must be borne in mind that dichlorotribromodimethyltetrahydrobenzene,  $C_8H_9Cl_2Br_3$ , on heating, loses two molecules of hydrogen bromide giving a dichlorobromo-*o*-xylene,  $CMe \leq \begin{smallmatrix} CMe:CCl \\ CH-CCl \end{smallmatrix} \geq CBr$ , the constitution of which has been definitely ascertained by synthesis (see page 277). It would appear from this fact that the bromine atom must become attached to the carbon atom between the two chlorine atoms, and this is explained by supposing that either substitution takes place, or more probably that bromine is first added on at the double linking, giving an unstable substance having the formula VI, which immediately loses hydrogen bromide. This loss may take place in several ways :



giving rise to substances with a double linking in different positions; but, as will be seen from the context, only two of these possibilities need be considered, namely, those involving the configurations VII and VIII, and from which the production of the above dichlorobromoxylene can be readily accounted for in the manner indicated by the following formulæ :



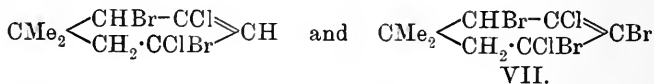
Now when dichlorotribromodimethyltetrahydrobenzene is oxidised with potassium permanganate, the sole products are bromoform and dimethylmalonic acid (thus definitely proving the presence of the *gem*-dimethyl group), the yield of the latter substance being 71 per cent. of that theoretically obtainable. It has been observed during the oxidation of many hydroaromatic substances containing halogen, that although they may be originally broken down at a double linking, the oxidation does not become completed until all those carbon atoms to which halogen atoms are attached in the original substance are either eliminated from the oxidation product or form part of a terminal carboxyl group; in other words, an acid obtained as an oxidation product is always free from halogen. For example, 5-bromo-1:1-dimethyl- $\Delta^3$ -tetrahydrobenzene (Trans., 1902, 81, 824) gives on oxidation  $\beta\beta$ -dimethylglutaric acid and not bromodimethyladipic acid:



Bearing this in mind, the formula which would best represent dichlorotribromodimethyltetrahydrobenzene would be VIII, for from a substance with formula VII dimethylsuccinic acid should result; but unfortunately the latter structure cannot be altogether excluded on these grounds.

The first product of the action of one molecule of bromine on dichlorodimethyldihydrobenzene is, for the foregoing reasons, supposed to have the following constitution:  $\text{CMe}_2 \begin{array}{c} \text{CHBr} - \text{CCl} \\ \text{CH}_2 \cdot \text{CClBr} \end{array} \text{CH}$ . This dichlorodibromodimethyltetrahydrobenzene is a liquid which cannot be purified, as on distillation either in air or in a vacuum it decomposes, evolving hydrogen bromide. In order to obtain some clue as to its constitution, the raw material in aqueous suspension was oxidised with potassium permanganate, when it became necessary to heat the mixture to the temperature of boiling water. The main product was dimethylmalonic acid, no trace of dimethylsuccinic acid being obtained, but the latter acid was produced in small quantities by carrying out the oxidation in cold acetone solution.

From a comparison of the formulæ of dichlorodibromo- and dichlorotribromodimethyltetrahydrobenzene, VII, it would appear that the substances represented by the formulæ



should give the same oxidation products, but the reactions are not strictly comparable on account of the greater stability of the latter

substance, which is not oxidised by potassium permanganate in the cold. This greater stability may be due simply to the presence of an additional halogen atom, or it may possibly point to the double linking being in a different position.

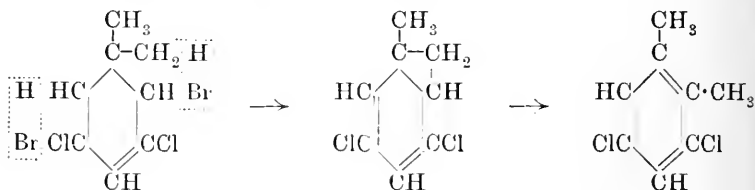
On referring to the oxidation of dichlorodimethyldihydrobenzene,  $\text{CMe}_2 \begin{smallmatrix} \text{CH}=\text{CCl} \\ \text{CH}_2 \cdot \text{CCl} \end{smallmatrix} \text{CH}$ , with potassium permanganate (Trans., 1902, 81, 829), it is seen that, when carried out at  $100^\circ$ , a mixture of dimethylmalonic and dimethylsuccinic acids is obtained, whereas if allowed to take place in the cold only the latter acid is formed. This proves fairly conclusively that if *as*-dimethylsuccinic acid can result as an oxidation product, the amount obtainable may be considerably lessened by carrying out the oxidation at a high temperature, since *as*-dimethylsuccinic acid is further oxidised to dimethylmalonic acid in similar cases when heat is employed.

If, therefore, dichlorotribromodimethyltetrahydrobenzene be represented by formula VII, it might be expected that some trace of *as*-dimethylsuccinic acid would have been obtained, which, however, was not the case; so that formula VIII seems the more probable, although this point is not quite definitely established.

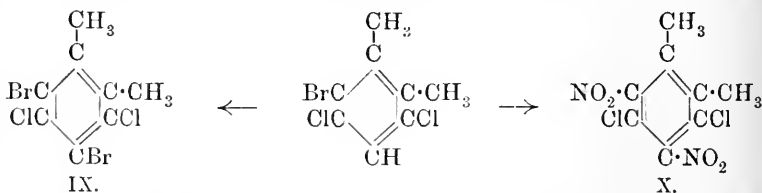
When dichlorotribromodimethyltetrahydrobenzene is heated with ordinary concentrated nitric acid, a somewhat unexpected reaction takes place, resulting in the formation of 3:5-dichloro-4:6-dibromo-*o*-xylene,  $\text{CH}_3 \cdot \text{C} \begin{smallmatrix} \text{C}(\text{CH}_3) \cdot \text{CCl} \\ \text{CBr}=\text{CCl} \end{smallmatrix} \text{CBr}$ , a substance which has also been synthetically prepared by the direct bromination of pure 3:5-dichloro-*o*-xylene. Its production in the above case is accounted for by supposing that, under the influence of heat, dichlorotribromodimethyltetrahydrobenzene first loses two molecules of hydrogen bromide forming 3:5-dichloro-4-bromo-*o*-xylene, which is then further brominated by the bromine liberated from the interaction of the concentrated nitric acid and hydrogen bromide.

As already mentioned, the product of the action of one molecule of bromine on dichlorodimethyldihydrobenzene is supposed to be dichlorodibromodimethyltetrahydrobenzene,  $\text{CMe}_2 \begin{smallmatrix} \text{CHBr}-\text{CCl} \\ \text{CH}_2 \cdot \text{CClBr} \end{smallmatrix} \text{CH}$ , but owing to the instability of this substance there does not seem to be any method of proving this supposition. As, however, it gives *as*-dimethylsuccinic acid on oxidation, it must contain the grouping  $\text{CMe}_2 \begin{smallmatrix} \text{C}- \\ \text{CH}_2 \cdot \text{C} \end{smallmatrix}$ . When heated, it evolves hydrogen bromide and gives as the two main products, 3:5-dichloro-*o*-xylene and 3:5-dichloro-6-bromo-*o*-xylene,  $\text{MeC} \begin{smallmatrix} \text{CMe} \cdot \text{CCl} \\ \text{CBr}=\text{CCl} \end{smallmatrix} \text{CH}$ .

The production of the former compound is readily explained by the loss of two molecules of hydrogen bromide:



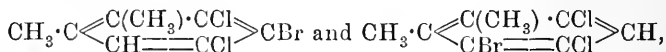
but at the present time no reasonable explanation can be offered for the formation of 3:5-dichloro-6-bromo-*o*-xylene, as in the case of the isomeric substance obtained by heating dichlorotribromodimethyltetrahydrobenzene. The reaction, which is more involved, is by no means quantitative, only 17—20 grams of the dichlorobromoxylene being obtained from the product of the action of bromine on 50 grams of dichlorodimethyldihydrobenzene. There can, however, be no doubt about the constitution of this substance, for in the first place it is shown to be a derivative of 3:5-dichloro-*o*-xylene, because on treatment with bromine it is quantitatively converted into 3:5-dichloro-4:6-dibromo-*o*-xylene (IX), identical with the substance produced by the direct bromination of pure 3:5-dichloro-*o*-xylene; and, further,



when treated with fuming nitric acid, it yields 3:5-dichloro-4:6-dinitro-*o*-xylene (X), identical with the compound obtained by the direct nitration of pure 3:5-dichloro-*o*-xylene.

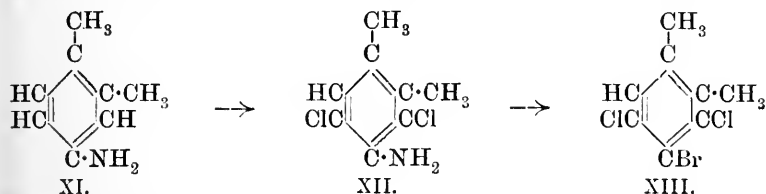
The only additional point to be decided is the position of the bromine atom, which is proved to be attached to the carbon atom 6 in the following manner.

There are but two possible forms of dichlorobromo-*o*-xylenes containing the chlorine atoms in the 3:5-position, and both these possibilities,

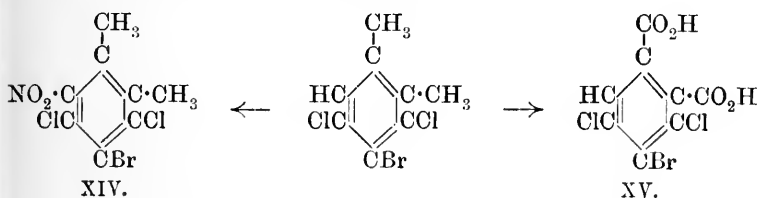


have been encountered in the course of this investigation. The best method for deciding between these seemed to consist in synthesis, and 4-*o*-xylidene (XI) was used as the starting point. This base, the constitution of which has been definitely established by the work of

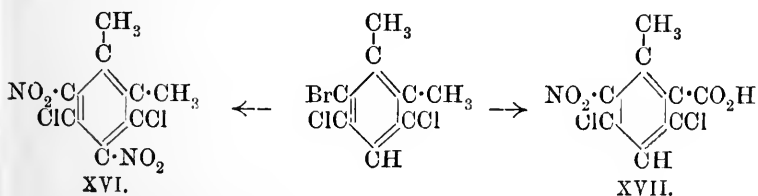
Jacobson (*Ber.*, 1884, 17, 159), when successively acetylated and treated with chlorine in glacial acetic acid solution, yields a dichloro-acetoxylidide, in which the chlorine atoms occupy the ortho-positions relatively to the amino-group. The corresponding dichloro-base, XII,



when diazotised in presence of cuprous bromide and hydrogen bromide, yields 3 : 5-dichloro-4-bromo-*o*-xylene (XIII), melting at 100°, and possessing all the characteristic properties and reactions of the compound obtained by the action of heat on dichlorotribromodimethyltetrahydrobenzene, thus proving that the substance obtained by heating dichlorodibromodimethyltetrahydrobenzene has the constitution of 3 : 5-dichloro-6-bromo-*o*-xylene. Both dichlorobromo xylenes give, on further bromination, one and the same dichlorodibromo-*o*-xylene, but in their behaviour towards nitric acid they differ markedly. When occupying position 4, the bromine atom is stable towards this reagent, but in position 6 it is readily replaced by a nitro-group. Thus, 3 : 5-dichloro-4-bromo-*o*-xylene gives, with fuming nitric acid, 3 : 5-dichloro-4-bromo-6-nitro-*o*-xylene (XIV), and, on oxidation with dilute nitric acid under pressure, is converted into 3 : 5-dichloro-4-bromo-*o*-phthalic acid (XV) :



whereas 3 : 5-dichloro-6-bromo-*o*-xylene gives, under similar conditions, respectively 3 : 5-dichloro-4 : 6-dinitro-*o*-xylene (XVI) and 3 : 5-dichloro-6-nitrotoluic acid (XVII).



## EXPERIMENTAL.

*Interaction of 3:5-Dichloro-1:1-dimethyl- $\Delta^4$ -dihydrobenzene with Two Molecules of Bromine.*

One hundred grams of freshly prepared dichlorodimethyldihydrobenzene (1 mol.) (Trans., 1902, 81, 826) were dissolved in 100 grams of dry chloroform, and 190 grams of bromine (2 mols.) added as rapidly as the comparative violence of the earlier stages of the reaction permitted. At first, the bromine was rapidly absorbed without the evolution of much hydrogen bromide, but subsequently, torrents of the gas were given off, and a quantity of a solid substance separated. The chloroform was then evaporated on the water-bath as quickly as possible\*, and the whole when left became semi-solid. It was filtered at the pump (Filtrate = A) and the solid residue (50 grams) purified by crystallisation from alcohol.

0.1388 gave 0.1176  $\text{CO}_2$  and 0.0368  $\text{H}_2\text{O}$ . C = 23.10; H = 2.94.

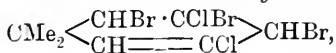
0.1442 „ 0.1220  $\text{CO}_2$  „ 0.0360  $\text{H}_2\text{O}$ . C = 23.07; H = 2.77.

0.1034 „ 0.2112 Ag haloids and 0.1340 Ag. Cl = 17.00; Br = 57.65.

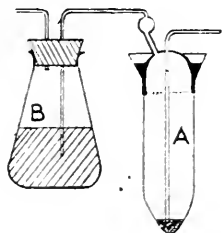
$\text{C}_8\text{H}_9\text{Cl}_2\text{Br}_3$  requires C = 23.07; H = 2.16; Cl = 17.07; Br = 57.69 per cent.

The high results obtained for the hydrogen are doubtless due to the fact that at its melting point this substance rapidly evolves hydrogen bromide, a small amount of which might find its way into the calcium chloride tube.

3:5-Dichloro-2:4:5-tribromo-1:1-dimethyl- $\Delta^5$ -tetrahydrobenzene,



is readily soluble in the cold in chloroform, benzene, or acetone, and in light petroleum or alcohol on warming; it crystallises from the latter solvent in stout, prismatic needles melting with evolution of gas at  $118^\circ$ .



*Action of Heat on Dichlorotribromodimethyl-tetrahydrobenzene.*—The action of heat on this compound was investigated in the apparatus given in the accompanying sketch, when it was found that the reaction is almost a quantitative one corresponding with the loss of two molecules of hydrogen bromide.

A weighed quantity of the substance was placed in the tube, A, which was heated at  $120$ — $125^\circ$  in a sulphuric

\* If the heating on the water-bath is continued for long, decomposition takes place, thus causing a considerable decrease in the amount of solid product.

acid bath and through which a slow current of dry air was drawn, thus causing the evolved hydrogen bromide to pass into the aqueous solution of silver nitrate contained in the flask, *B*. When no more gas was given off from the molten substance, the contents of *B* were filtered, dried, and weighed.

0.5138 gave 0.4466 AgBr.  $\text{HBr} = 37.45$ .

$\text{C}_8\text{H}_9\text{Cl}_2\text{Br}_3$ , when losing  $2\text{HBr}$ , requires  $\text{HBr} = 38.94$  per cent.

The residue in *A* solidified on cooling, and was proved by the following facts to be identical with the 3:5-dichloro-4-bromo-*o*-xylene described on p. 275; it crystallised from alcohol in masses of felt-like needles melting at  $99-100^\circ$ .

0.1148 gave 0.2140 Ag haloids. Halogen = 59.26.

$\text{C}_8\text{H}_7\text{Cl}_2\text{Br}$  requires Ag haloids = 187.0. Halogen = 59.44 per cent.

Moreover, on treatment with bromine in the presence of iron, it gave 3:5-dichloro-4:6-dibromo-*o*-xylene melting at  $233^\circ$  (see page 284), and fuming nitric acid converted it into 3:5-dichloro-4-bromo-6-nitro-*o*-xylene melting at  $176^\circ$  (see page 275).

*Action of Nitric Acid on Dichlorotribromodimethyltetrahydrobenzene.*

Five grams of the tetrahydrobenzene derivative and 40 c.c. of nitric acid (sp. gr. 1.42) were placed in a flask with a ground-glass stopper attached to a condenser. No reaction took place in the cold, so the mixture was heated on a water-bath, when the solution soon became coloured and quantities of nitrous fumes and bromine were evolved. The solid was quickly converted into an oil, which gradually resolidified in flakes. After heating for ten minutes, the contents of the flask were poured into water, filtered, spread on porous plate, and the residue (2.5 grams) crystallised from ethyl acetate. The needles so obtained melted at  $233^\circ$ , and the melting point was not altered on mixing with the 3:5-dichloro-4:6-dibromo-*o*-xylene described on page 284; and that these two substances are identical is conclusively proved by the following analytical figures:

0.1566 gave 0.1670  $\text{CO}_2$  and 0.0268  $\text{H}_2\text{O}$ .  $\text{C} = 29.08$ ;  $\text{H} = 1.89$ .

0.2006 „ 0.4012 Ag haloids and 0.2617 Ag.  $\text{Cl} = 21.65$ ;  $\text{Br} = 47.94$ .  
 $\text{C}_8\text{H}_6\text{Cl}_2\text{Br}_2$  requires  $\text{C} = 28.83$ ;  $\text{H} = 1.80$ ;  $\text{Cl} = 21.32$ ;  $\text{Br} = 48.05$  per cent.

The ethyl acetate mother liquors contained a small quantity of a more fusible solid; this substance and the small oily residue obtained on evaporating the aqueous filtrate from the raw material were not further investigated.

*Oxidation of Dichlorotribromodimethyltetrahydrobenzene.*—Twenty

grams of the substance were suspended in 500 c.c. of water and heated on the water-bath in a flask attached to a reverse condenser, and 60 grams of finely powdered potassium permanganate added in small portions at a time. After heating for ten hours, practically all the permanganate had been used up and the whole was distilled in steam, when a small amount of bromoform passed over. The residue was filtered from manganese dioxide, the filtrate evaporated to a small bulk, acidified, and extracted ten times with ether. The ethereal solution, on evaporation, left a residue weighing 4.5 grams, whereas the amount calculated for the production of dimethylmalonic acid is 6.3 grams. This residue rapidly solidified and melted at 187—188°; after one crystallisation from water, it melted at 190° with evolution of gas.

0.1412 gave 0.2346  $\text{CO}_2$  and 0.0778  $\text{H}_2\text{O}$ .  $\text{C} = 45.31$ ;  $\text{H} = 6.12$ .

$\text{C}_5\text{H}_8\text{O}_4$  requires  $\text{C} = 45.45$ ;  $\text{H} = 6.06$  per cent.

In order to prove more completely the identity of this substance with dimethylmalonic acid, the remainder was heated in a distillation flask, when carbon dioxide was evolved, and a colourless liquid with the unmistakable odour of isobutyric acid passed over, a portion of the liquid was converted into the silver salt.

0.1412 gave 0.0788 Ag.  $\text{Ag} = 55.80$ .

$\text{C}_4\text{H}_7\text{O}_2\text{Ag}$  requires  $\text{Ag} = 55.38$  per cent.

After finding that dichlorodibromodimethyltetrahydrobenzene gave dimethylsuccinic acid on oxidation with potassium permanganate in acetone solution (see page 283), the oxidation of dichlorotribromodimethyltetrahydrobenzene was repeated, using boiling acetone as solvent, the reaction being carried out as described on page 283. The crude oxidation product melted at 189—190° with evolution of gas and formation of isobutyric acid, and therefore consisted of dimethylmalonic acid, no trace of dimethylsuccinic acid being obtained.

*Examination of the Filtrate A* (see page 272).—On distilling this liquid either in air or in a vacuum, a violent evolution of hydrogen bromide took place, and the main fraction (260—270° under 764 mm.) solidified completely on cooling to a waxy substance melting at 85—90°. Considerable difficulty was experienced in purifying this material, and it was only after repeated crystallisation from absolute alcohol that a substance melting at 98—99° was obtained.

A better method for the isolation of this substance in a pure condition consists in allowing the liquid A to remain in a vacuum over caustic potash, when it gradually solidifies to a semi-solid cake, the mother liquor being again placed in a vacuum, when more solid

separated. By repeating this process, 65 grams of a crystalline compound were obtained melting at 95—97°, and which, after recrystallisation from alcohol, melted sharply at 100°.

0.1884 gave 0.2594 CO<sub>2</sub> and 0.0470 H<sub>2</sub>O. C = 37.55; H = 2.77.

0.1083 „ 0.2004 Ag haloids and 0.1364 Ag. Cl = 27.27; Br = 31.82. C<sub>8</sub>H<sub>7</sub>Cl<sub>2</sub>Br requires C = 37.79; H = 2.75; Cl = 27.95; Br = 31.49 per cent.

3 : 5-Dichloro-4-bromo-o-xylene, CH<sub>3</sub>·C<math display="block">\begin{array}{c} \text{C}(\text{CH}\_3) : \text{CCl} \\ \text{CH} \text{---} \text{CCl} \end{array}\text{CBr}, is readily soluble in the cold in light petroleum (b. p. 80—100°), chloroform, benzene, ether, or acetone, and in glacial acetic acid or alcohol on warming. It crystallises from alcohol in long, felt-like needles (compare the properties of 4 : 5-dichloro-6-bromo-o-xylene, Claus and Kronweg, *J. pr. Chem.*, 1891, [ii], 43, 259), which, on pressing, form a waxy material melting at 100° and resolidifying at 98°. It distils without decomposition at 170—175° under 30 mm., and at 265—270° under the ordinary pressure, and is volatile in steam.

*Action of Bromine on 3 : 5-Dichloro-4-bromo-o-xylene.*—The substance was dissolved in a small quantity of chloroform, and bromine added in presence of iron filings. On warming, substitution readily took place, and the resulting solid crystallised from ethyl acetate in glistening needles melting at 233—233.5°, the melting point remaining unaltered when the substance was mixed with pure 3 : 5-dichloro-4 : 6-dibromo-o-xylene (see page 284), thus proving the identity of these two substances. The yield is quantitative.

*Action of Nitric Acid on 3 : 5-Dichloro-4-bromo-o-xylene.*—Three grams of dichlorobromoxylene were added to 40 c.c. of fuming nitric acid and warmed on the water-bath, when the solid gradually dissolved. The heating was continued for 20 minutes, when the mixture was poured into water, and the separated solid (2.6 grams) crystallised from alcohol. The crystals melted at 175—176°, and were thought to be identical with the 3 : 5-dichloro-4 : 6-dinitro-o-xylene (m. p. 175—176°), described on page 284, but a mixture of the two substances melted at 154—155°, thus proving that its components were dissimilar. After a further crystallisation of the above material, the nitrogen was determined.

0.2580 gave 10.2 c.c. moist nitrogen at 23° and 772 mm. N = 4.52.

C<sub>8</sub>H<sub>6</sub>O<sub>2</sub>NCl<sub>2</sub>Br requires N = 4.68 per cent.

3 : 5-Dichloro 4-bromo-6-nitro-o-xylene, CH<sub>3</sub>·C<math display="block">\begin{array}{c} \text{C}(\text{CH}\_3) : \text{CCl} \\ \text{C}(\text{NO}\_2) - \text{CCl} \end{array}\text{CBr}, is readily soluble in the cold in chloroform, benzene, acetone, ethyl acetate, or ether, and crystallises from dilute acetic acid or alcohol in faintly yellow, glistening needles melting at 175.5—176.5°.

*Oxidation of 3 : 5-Dichloro 4 bromo-o-xylene.*—Eight grams of the dichlorobromoxylene were heated in quantities of two grams at a time, with 15 c.c. of nitric acid (sp. gr. 1.15), in sealed tubes for 7 hours at 180—200°. The contents of the tubes, which were entirely liquid, were evaporated *in vacuo*, when 9 grams of a white solid, giving a marked fluorescein reaction, were obtained. On testing the solubilities, it was found that this substance would crystallise from xylene, and the whole was therefore boiled with this solvent, when it slowly dissolved, but on cooling only 0.9 gram separated (see page 277). The mother liquors were evaporated, and the solid residue purified by crystallisation from a mixture of benzene and light petroleum.

0.1592 gave 0.1880 CO<sub>2</sub> and 0.0084 H<sub>2</sub>O. C = 32.20 ; H = 0.58.

0.1042 „ 0.1667 Ag haloids and 0.1134 Ag. Cl = 23.50 ; Br = 27.63.  
C<sub>8</sub>H<sub>3</sub>O<sub>3</sub>Cl<sub>2</sub>Br requires C = 32.43 ; H = 0.34 ; Cl = 23.98 ; Br = 27.02  
per cent.



3 : 5-Dichloro-4-bromo-o-phthalic anhydride,  $\text{OC} \cdot \text{C} \begin{array}{l} \nearrow \text{C} = \text{CCl} \\ \searrow \text{CH} \cdot \text{CCl} \end{array} \text{CBr}$

is readily soluble in the cold in benzene, chloroform, acetone, and ethyl acetate, soluble with difficulty in alcohol and light petroleum, and crystallises from a mixture of benzene and light petroleum in radiating clusters of stumpy needles melting at 170—171°. It can be sublimed unchanged in feathery needles and gives a most marked fluorescein reaction. Its method of preparation from the corresponding acid by boiling with xylene is somewhat unusual, but presumably the temperature of boiling xylene is sufficiently high to cause the formation of anhydride, and at the same time supplies a ready means for separating the acid from the nitrogenous substance (see p. 277), which is also produced in small quantity during the oxidation.

In a second preparation, the anhydride was produced by heating the crude oxidation product with acetyl chloride, &c. The solid so obtained was found to contain nitrogen, but on submitting it to a process of sublimation, the nitrogenous substance was decomposed, whilst the sublimate, after crystallisation, melted at 169—170° and consisted of pure 3 : 5-dichloro-4-bromo-o-phthalic anhydride.

The anhydride is not acted on by cold water, but dissolves slowly in the boiling solvent, and on evaporating the solution the corresponding *acid* remains ; this substance is readily soluble in the cold in water, alcohol, and acetone, but dissolves readily in boiling chloroform or benzene ; it crystallises from water saturated with hydrogen chloride in small, flattened needles melting at 169—170° with previous diminution in bulk and partial sublimation. Unless purified in this way through the anhydride, the acid melts much lower (156—162°) with vigorous evolution of gas.

A portion of the pure acid was converted into the silver salt, which is a white, caseous precipitate.

0.2000 gave 0.0817 Ag.  $\text{Ag} = 40.85$ .

$\text{C}_8\text{HO}_4\text{Cl}_2\text{BrAg}_2$  requires  $\text{Ag} = 40.91$  per cent.

The *anil* was obtained by dissolving the anhydride in benzene and adding the calculated amount of aniline, when a precipitate was at once formed, which was filtered and dried. When heated, it melts at  $120\text{--}125^\circ$  with evolution of gas, then resolidifies, and, finally, again melts at  $180\text{--}195^\circ$ , at which temperature it was maintained until no more gas was evolved. The solid thus obtained readily dissolved in cold benzene or chloroform, but was not readily soluble in alcohol even on boiling; it crystallised from acetone or ethyl acetate in masses of glistening, silken needles melting at  $200\text{--}200.5^\circ$ .

0.2638 gave 8.6 c.c. moist nitrogen at  $14^\circ$  and 762 mm.  $\text{N} = 3.84$ .

$\text{C}_{14}\text{H}_6\text{O}_2\text{NCl}_2\text{Br}$  requires  $\text{N} = 3.77$  per cent.

It was mentioned on page 276 that on crystallising the crude oxidation product from xylene, only 0.9 gram of solid separated, which, on examination, was found to contain nitrogen.

0.1990 gave 8.6 c.c. moist nitrogen at  $18^\circ$  and 768 mm.  $\text{N} = 5.05$ .

$\text{C}_8\text{H}_3\text{O}_6\text{NCl}_2$  requires  $\text{N} = 5.00$  per cent.

This substance is in all probability 3:5-dichloro-4-nitro-o-phthalic acid, as in a halogen determination the proportion of silver in the total silver haloids showed conclusively that the substance could not contain any bromine. The acid is very readily soluble in the cold in water, alcohol, ethyl acetate, and acetone, almost insoluble in chloroform and benzene on boiling, and crystallises from xylene in clusters of flattened needles melting at  $165^\circ$  with a brisk evolution of gas.

#### *Synthesis of 3:5-Dichloro-4-bromo-o-xylene.*

The 4-o-xylylidine used in these experiments melted sharply at  $49^\circ$ , and gave an acetyl derivative crystallising from dilute alcohol in long, glistening needles melting at  $99^\circ$  (compare Jacobson, *Ber.*, 1884, 17, 161).

The acetoxylylidiide, in quantities of 5 grams, was dissolved in 10 c.c. of glacial acetic acid, the whole cooled in ice, and dry chlorine passed in until the gain in weight corresponded with the substitution of two hydrogen atoms by chlorine. A crust of white, nodular crystals then slowly separated, which was drained from excess of acetic acid and placed in water. At first, the substance became semi-liquid, part dissolving, and then the whole mass resolidified, the solid being

purified by crystallising from dilute alcohol until the melting point of the glistening scales which separated was about  $185^{\circ}$ . The yield is small, being 15—20 per cent. of the theoretical.

No attempt was made to isolate a pure acetyl derivative, and the substance melting at about  $185^{\circ}$  was directly hydrolysed by boiling for 3—4 hours with concentrated hydrochloric acid; the solid product was suspended in dilute caustic potash and distilled in steam, when an oil passed over which soon solidified. The crude material melted for the most part at  $50^{\circ}$ , but did not become clear until  $95^{\circ}$ , and was found to consist of two substances which could be easily separated by means of their different solubilities in alcohol. The whole was dissolved in the smallest possible quantity of hot absolute alcohol, when on cooling a few long, needle-shaped crystals separated, melting at  $170^{\circ}$ . The filtrate from these crystals (which were not further investigated) was diluted with water, when glistening needles separated, which melted for the most part at  $43\text{--}45^{\circ}$ , but did not become quite clear until  $85^{\circ}$ . After repeating the above process of purification, a substance was obtained melting sharply at  $44.5^{\circ}$ , and in this the chlorine was determined.

0.1028 gave 0.1560 AgCl. Cl = 37.54.

$\text{C}_8\text{H}_9\text{NCl}_2$  requires Cl = 37.37 per cent.

3 : 5-Dichloro-4-o-xylylidine,  $\text{CH}_3 \cdot \text{C} \begin{array}{c} \nwarrow \text{C}(\text{CH}_3) : \text{CCl} \\ \searrow \text{CH} \text{---} \text{CCl} \end{array} \text{C} \cdot \text{NH}_2$ , is extremely soluble in the cold in light petroleum (b. p.  $40\text{--}60^{\circ}$ ), chloroform, acetone, benzene, or ether, and crystallises from dilute alcohol in long, glistening, silken needles melting at  $44.5^{\circ}$ .

In order to replace the amino-group by bromine, the base was suspended in hydrobromic acid (sp. gr. 1.45), in which it is not at all readily soluble, a solution of freshly prepared cuprous bromide in hydrobromic acid added, and slightly more than the calculated quantity of sodium nitrite dissolved in the smallest possible amount of water dropped into the mixture, which was heated on the water-bath to a temperature of  $60\text{--}70^{\circ}$ . After one hour, the whole was distilled in steam, when a solid passed over which melted at  $95\text{--}97^{\circ}$ , and proved to be identical in every respect with the dichlorobromoxylene described on page 275. It crystallised from absolute alcohol in long, glistening, felt-like needles melting at  $100^{\circ}$ , which, on pressing together, assume a waxy consistency. When brominated in the presence of iron filings, it gave a dichlorodibromoxylene crystallising from ethyl acetate in glistening, silken needles melting at  $233^{\circ}$ , a melting point which remained unaltered on mixing with the 3 : 5-dichloro-4 : 6-dibromo-o-xylene described on page 284. Fuming nitric acid slowly dissolves the substance on warming, and on pouring the solution into water a solid separated which crystallised from alcohol in pale yellow, glistening

needles melting at 175—176°, and giving the same melting point when mixed with the dichlorobromonitroxylene described on page 275.

*Interaction of 3:5-Dichloro-1:1-dimethyl- $\Delta^2$ -<sup>4</sup>-dihydrobenzene with One Molecule of Bromine.*

Dichlorodimethyldihydrobenzene (1 molecule) was dissolved in three times its weight of dry chloroform and dry bromine (1 molecule) gradually added, the whole being cooled in ice. The bromine is readily absorbed, hardly any hydrogen bromide being evolved, and a sharp end point is noticed when one molecule of bromine has been used up. On evaporating the chloroform, a light yellow liquid remained, which, as it showed no signs of solidification even after a long time, was distilled, when torrents of hydrogen bromide were evolved, and a clear yellow, refractive liquid, boiling between 200° and 270°, passed over. On submitting the liquid to careful and repeated fractional distillation, two main fractions were obtained, boiling at 220—230° and 240—250°. All the intermediate fractions slowly deposited crystals which were found to be identical with the 3:5-dichloro-6-bromo-*o*-xylene contained in the fraction 240—250° (see page 280).

*The Fraction 220—230° contained 3:5-Dichloro-*o*-xylene* (Trans., 1902, 81, 1534).

This liquid was again fractionated, and a portion, boiling at 226°, was found to solidify on cooling and melted at 3—4°. When treated with bromine in presence of iron filings, it gave 3:5-dichloro-4:6-dibromo-*o*-xylene melting at 233° (see page 284), and on nitration gave 3:5-dichloro-4:6-dinitro-*o*-xylene melting at 175° (see page 284).

As a further proof of the presence of 3:5-dichloro-*o*-xylene, some of the liquid was oxidised with dilute nitric acid under pressure (compare Trans., 1902, 81, 1536). On opening the tube, it was found to contain a quantity of long, silken needles floating in a liquid; these were filtered (Filtrate = A), purified by crystallisation from dilute acetic acid, and the chlorine determined.

0.1088 gave 0.1544 AgCl. Cl = 35.10.

$C_8H_6O_2Cl_2$  requires Cl = 34.63 per cent.

The acid was also titrated against *N*/10 sodium hydroxide with the following result.

0.4350 required 21.94 c.c. *N*/10 solution = 0.0877 NaOH.

$C_8H_6O_2Cl_2$  requires 0.0849 NaOH.

This substance, which is evidently a *dichlorotoluic acid*, readily dissolves in the cold in potassium hydroxide, alcohol, acetone, ethyl acetate, or benzene, and is not readily soluble even on boiling in light petroleum or water; it crystallises from dilute acetic acid in long, glistening needles melting at 184—185°.

The production of this dichlorotoluic acid was never observed during the preparation of 3:5-dichloro-*o*-phthalic acid (Trans., *ibid.*). This may be accounted for by the facts that in the above oxidation rather less nitric acid was used than formerly, and that the sealed tube was not heated for so many hours. It is intended to repeat the oxidation of 3:5-dichloro-*o*-xylene in the hope of obtaining the above dichlorotoluic acid, and definitely proving its constitution.

The filtrate A (see above) was evaporated *in vacuo*, when a white solid remained which gave a very marked fluorescein reaction. The anhydride prepared from it by treatment with acetyl chloride crystallised from light petroleum in radiating clusters of glistening needles melting at 89°, the melting point remaining unaltered on mixing the compound with the anhydride of 3:5-dichloro-*o*-phthalic acid, with which the substance is evidently identical.

The *fraction* 240—250°, which solidified completely (17—20 grams from 50 grams of dichlorodimethyldihydrobenzene), was spread on porous plate and purified by crystallisation from ethyl alcohol.

0.1546 gave 0.2161 CO<sub>2</sub> and 0.0408 H<sub>2</sub>O. C = 38.12; H = 2.93.

0.1040 gave 0.1954 Ag haloids and 0.1334 Ag. Cl = 28.23; Br = 31.38. C<sub>8</sub>H<sub>7</sub>Cl<sub>2</sub>Br requires C = 37.79; H = 2.75; Cl = 27.95; Br = 31.49 per cent.

3:5-Dichloro-6-bromo-*c*-xylene,  $\text{CH}_3 \cdot \text{C} \begin{array}{c} \text{C}(\text{CH}_3) \cdot \text{CCl} \\ \text{CBr} \text{---} \text{CCl} \end{array} \text{CH}$ , is readily soluble in the cold in benzene, acetone, light petroleum, or ethyl acetate, crystallises from ethyl or methyl alcohol in long, slender, glistening needles melting at 42°, and can be distilled in air without undergoing any decomposition. It does not decolorise a chloroform solution of bromine, but in the presence of iron filings substitution takes place readily. The solid product crystallised from ethyl acetate in long, glistening needles melting at 233°, and was identical with the 3:5-dichloro-4:6-dibromo-*o*-xylene described on page 284.

*Action of Nitric Acid on 3:5-Dichloro-6-bromo-*o*-xylene.*—Two grams of the substance were gradually added to 10 c.c. of fuming nitric acid, when it readily dissolved, and the solution became warm. The whole was heated on the water-bath for 20 minutes, poured into water, the separated solid filtered, and crystallised from alcohol. It separated in pale yellow, four-sided plates melting at 174—175°, and proved to be in every way identical with the 3:5-dichloro-4:6-dinitro-*o*-xylene described on page 284.

0.2256 gave 20.0 c.c. moist nitrogen at  $19^{\circ}$  and 760 mm.  $N = 10.20$ .  
 $C_8H_6O_4N_2Cl_2$  requires  $N = 10.56$  per cent.

*Oxidation of 3:5-Dichloro-6-bromo-o-xylene.*—The substance was oxidised by heating it in quantities of 2 grams at a time with 15 c.c. of dilute nitric acid (sp. gr. 1.15) for 6 hours at  $180-190^{\circ}$ . The contents of the tube, consisting of white, needle-shaped crystals suspended in a greenish-brown liquid, were filtered (filtrate A), the solid treated with potassium hydroxide, in which a slight amount was insoluble, filtered, reprecipitated with sulphuric acid, and purified by crystallisation from water.

0.2042 gave 9.8 c.c. moist nitrogen at  $22^{\circ}$  and 770 mm.  $N = 5.51$ .  
 $C_8H_5O_4NCl_2$  requires  $N = 5.6$  per cent.

The acid was then titrated against  $N/10$  sodium hydroxide.

0.3952 required 16.2 c.c.  $N/10$  solution = 0.0648 NaOH.  
 $C_8H_5O_4NCl_2$  requires 0.0632 NaOH.

*3:5-Dichloro-6-nitrotoluic acid* is readily soluble in the cold in aqueous potassium hydroxide, alcohol, acetone, and ethyl acetate, less so in benzene or chloroform, and crystallises from water in feathery needles melting at  $187-189^{\circ}$ .

The filtrate A (see above) yielded on evaporation a solid which gave the fluorescein reaction in a marked degree, but the amount was too small for complete investigation.

As the light yellow liquid (see page 279) obtained by the action of one molecule of bromine on dichlorodimethyldihydrobenzene and presumably *dichlorodibromodimethyltetrahydrobenzene* cannot be distilled even in a vacuum without decomposition, it was submitted to oxidation with potassium permanganate in order to obtain some evidence as to its constitution.

For this purpose, 50 grams of the substance were suspended in 700 c.c. of water, 90 grams of finely-powdered potassium permanganate gradually added, and the whole heated on the water-bath in a flask attached to a reflux condenser. At first, the oxidation is vigorous, and some bromine is liberated, but it soon becomes much less active, and the permanganate is very slowly decolorised, in the above case requiring 10 hours. The contents of the flask were then filtered, when some oil passed through with the filtrate (= A), which was extracted with ether (extract = B). The residual manganese dioxide was then suspended in water and distilled in steam, when an oil passed over with the aqueous distillate, and this was extracted with ether (extract = C).

A. The filtrate was evaporated to a small bulk, acidified, and re-

peatedly extracted with ether, when 3.5 grams of a solid having a marked odour of fatty acids were obtained. On crystallisation from water, a slab of crystals separated, which melted at 190—191° with brisk evolution of gas, and consisted of dimethylmalonic acid, for on distillation, *isobutyric* acid was obtained boiling at 153—155°. A portion of this acid was converted into the silver salt.

0.1888 gave 0.1046 Ag.  $\text{Ag} = 55.40$ .

$\text{C}_4\text{H}_7\text{O}_2\text{Ag}$  requires  $\text{Ag} = 55.38$  per cent.

The mother liquors from the dimethylmalonic acid were evaporated to dryness and distilled, when a further quantity of *isobutyric* acid was obtained, and at a much higher temperature 0.5 gram of a liquid passed over which at once solidified. This solid was insoluble in cold water but dissolved on boiling, and after saturating the solution with hydrogen chloride, needle-shaped crystals separated, melting at 164° with evolution of gas. These crystals gave the fluorescein reaction in a marked degree and evidently consisted of 3:5-dichloro-*o*-phthalic acid, for on heating with acetyl chloride they were converted into an anhydride which crystallised from light petroleum in glistening, flattened needles melting at 89°; this melting point was not altered on mixing the substance with pure 3:5-dichloro-*o*-phthalic anhydride (compare *Trans.*, 1902, 81, 1536).

*B.* This extract, which weighed 9 grams, slowly deposited crystals. These were filtered and crystallised from alcohol, when the compound separated in stout needles, which melted with evolution of gas at 118° and were proved by the following facts to be identical with the dichlorotribromodimethyltetrahydrobenzene described on page 272.

0.2184 gave 0.4472 Ag haloids.  $\text{Halogen} = 74.81$ .

$\text{C}_8\text{H}_9\text{Cl}_2\text{Br}_3$  requires halogen = 74.75 per cent.

This substance, when warmed with concentrated nitric acid, yielded 3:5-dichloro-4:6-dibromo-*o*-xylene melting at 233° (see page 273). The liquid from which the above crystals had separated was distilled in air, when hydrogen bromide was evolved and two fractions were obtained boiling at 220—230° and 240—250°. The first of these fractions contained 3:5-dichloro-*o*-xylene, and the latter, on cooling, solidified almost completely to a solid which melted at 42°, and was identical with the 3:5-dichloro-6-bromo-*o*-xylene mentioned on page 280.

*C.* The oil deposited a small quantity of solid, readily soluble in the ordinary organic solvents with the exception of light petroleum and alcohol; from these solutions, the compound separated in fern-like aggregates of flattened needles melting at 143—144°. The crystals, which contained halogen, did not decolorise a chloroform solution of

bromine, and were readily oxidised by potassium permanganate on warming, but the amount was too small for a determination of their constitution.

The results of this oxidation, although appearing somewhat complicated, are easily explained. The temperature to which the mixture is heated evidently causes the partial decomposition of the original substance into hydrogen bromide, 3:5-dichloro-*o*-xylene, and 3:5-dichloro-6-bromo-*o*-xylene, from the second of which, on further oxidation, there results 3:5-dichloro-*o*-phthalic acid. Moreover, the liberated hydrogen bromide would, in contact with potassium permanganate, evolve bromine, which would act on some of the original material to give dichlorotribromodimethyltetrahydrobenzene.

The oxidation was then repeated, using acetone as solvent instead of water. Fifty grams of crude dichlorodibromodimethyltetrahydrobenzene (page 279) were dissolved in a mixture of 500 c.c. pure acetone and 100 c.c. of water, and 110 grams of finely-powdered potassium permanganate gradually added. The first stages of the oxidation were accompanied by a considerable evolution of heat, so much so that the mixture was cooled in ice-water, and later, when the oxidation became less vigorous, it was allowed to take place at the ordinary atmospheric temperature. When the permanganate had been used up, the product was filtered and the acetone evaporated, when 6 grams of an oil separated which was not further examined. After removing the oil by filtration, the filtrate was evaporated to a small bulk, acidified with sulphuric acid, extracted ten times with ether, and the ether evaporated, when a residue weighing 9 grams was obtained, which slowly solidified. The solid melted for the most part at 120–125°, but did not become clear until 150°, when a gas was evolved. This is the manner in which a mixture of dimethylmalonic and *α*-dimethylsuccinic acids behaves on heating in a capillary tube as already observed (Trans., 1902, 81, 829). The solid was therefore heated at 180° in a distillation flask until no more gas was given off, during which time a liquid distilled over which proved to be *isobutyric* acid.

The liquid residue in the distillation flask was insoluble in cold water, but dissolved on boiling, and after saturating the solution with hydrogen chloride, needle-shaped crystals separated melting at 140–141°.

0.1178 gave 0.2128 CO<sub>2</sub> and 0.0746 H<sub>2</sub>O. C = 49.26; H = 7.03.

C<sub>6</sub>H<sub>10</sub>O<sub>4</sub> requires C = 49.31; H = 6.85 per cent.

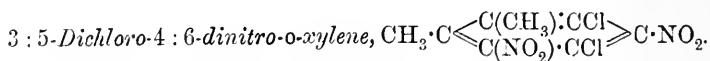
The identity of this substance with *α*-dimethylsuccinic acid was further proved by the preparation from it of an anilic acid, which

crystallised from methyl alcohol in flattened, nacreous needles melting at 186—187°.

Incidentally, it was observed that *as*-dimethylsuccinic acid gives a particularly brilliant fluorescein reaction.

*Derivatives of 3:5-Dichloro-o-xylene.*

The following derivatives were prepared from pure 3:5-dichloro-o-xylene (Trans., 1902, 81, 1533) for the purpose of comparison with substances encountered in the course of this investigation.

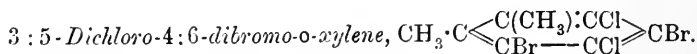


On adding 3:5-dichloro-o-xylene to a mixture of fuming nitric and concentrated sulphuric acids, much heat is evolved, and a solid separates almost at once. The whole was heated on the water-bath for ten minutes, poured into a large volume of water, filtered, and after purifying the residue by crystallisation from alcohol, the nitrogen was determined.

0.2550 gave 22.8 c.c. moist nitrogen at 20° and 772 mm. N = 10.39.

$\text{C}_8\text{H}_6\text{O}_4\text{N}_2\text{Cl}_2$  requires N = 10.56 per cent.

3:5-Dichloro-4:6-dinitro-o-xylene is readily soluble in the cold in chloroform, acetone, ether, benzene, or ethyl acetate, and crystallises from dilute acetic acid or alcohol in faintly yellow, glistening, four-sided crystals melting at 175—176°.



This substance is readily obtained by brominating 3:5-dichloro-o-xylene in presence of a small quantity of iron filings. It is soluble in the cold in benzene and chloroform, sparingly so in alcohol, even on boiling, and crystallises from light petroleum (b. p. 80—100°), acetone, or ethyl acetate in slender, glistening needles melting at 233—233.5°. It sublimes in stout needles without decomposition.

0.1039 gave 0.2088 mixed haloids and 0.1362 Ag. Cl = 21.65; Br = 48.12.

$\text{C}_8\text{H}_6\text{Cl}_2\text{Br}_2$  requires Cl = 21.32; Br = 48.05 per cent.

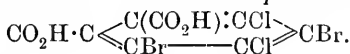
The mother liquors from the crystallisation of this derivative contained a substance of much lower melting point (100—118°), which from its appearance and properties must have consisted for the most

part of 3 : 5-dichloro-4-bromo-*o*-xylene, but although repeatedly crystallised, it was not found possible to isolate a substance of constant melting point.

The action of one molecule of bromine on 3 : 5-dichloro-*o*-xylene was also investigated, because Claus (*J. pr. Chem.*, [ii], 42, 125) attempted to prepare a dichlorobromoxylene by the action of one molecule of bromine on dichloro-*m*-xylene, but found that under these conditions one half of the substance was converted into the dichlorodibromoxylene, whilst the residue remained unchanged.

When 3 : 5-dichloro-*o*-xylene is treated with one molecule of bromine in presence of iron filings, a very small amount of unaltered material is recovered, and on submitting the solid obtained to fractional crystallisation from alcohol, it was found to consist principally of 3 : 5-dichloro-4-bromo-*o*-xylene, melting at 100° (see page 275). Some dichlorodibromoxylene (m. p. 233°) is also produced, from which it is almost impossible to separate the dichlorobromoxylene in a pure condition. Undoubtedly the latter substance is most easily obtained pure by the elimination of hydrogen bromide from dichlorotribromodimethyltetrahydrobenzene (see page 274).

3 : 5-Dichloro-4 : 6-dibromo-*o*-phthalic Acid,



This acid may be prepared by heating the above dichlorodibromoxylene in quantities of two grams at a time with 15 c.c. of dilute nitric acid (sp. gr. 1.15) in sealed tubes at a temperature of 230—240° for six hours. Experiment showed that this strength of nitric acid had little or no action on the dichlorodibromoxylene at a temperature of 190—200°, even after heating for 7 hours; with more concentrated nitric acid, considerable quantities of acids containing nitrogen were produced, and these were difficult to remove from the desired phthalic acid.

The semi-solid contents of the tubes were filtered and the residue extracted two or three times with boiling water, in which solvent any unchanged dichlorodibromoxylene is quite insoluble. On cooling the filtrate, the phthalic acid separated, and was purified by further crystallisation from water.

0.1622 gave 0.1444 CO<sub>2</sub> and 0.0126 H<sub>2</sub>O. C = 24.27; H = 0.86.

C<sub>8</sub>H<sub>2</sub>O<sub>4</sub>Cl<sub>2</sub>Br<sub>2</sub> requires C = 24.42; H = 0.51 per cent.

3 : 5-Dichloro-4 : 6-dibromo-*o*-phthalic acid is readily soluble in the cold in alcohol, acetone, and ethyl acetate, insoluble even on boiling in light petroleum or chloroform, and crystallises from water in small,

shining scales, which, on heating, sinter and partially sublime, and finally melt at  $240-241^{\circ}$  with evolution of gas. It gives a very marked fluorescein reaction, and, when heated between two watch glasses, sublimes in feathery needles, which were found to consist of the anhydride.

The *anhydride* was prepared by heating the acid with excess of acetyl chloride for one hour, evaporating the solvent, and crystallising the residue from acetic anhydride.

0.2016 gave 0.1930  $\text{CO}_2$  and 0.0014  $\text{H}_2\text{O}$ .  $\text{C} = 26.10$ ;  $\text{H} = 0.00$ .

0.1032 ,, 0.1834 mixed haloids and 0.1198 Ag.  $\text{Cl} = 19.40$ ;  
 $\text{Br} = 42.21$ .

$\text{C}_8\text{O}_3\text{Cl}_2\text{Br}_2$  requires  $\text{C} = 25.60$ ;  $\text{H} = 0.00$ ;  $\text{Cl} = 18.93$ ;  $\text{Br} = 42.67$   
per cent.

The anhydride readily dissolves in the cold in benzene and ethyl acetate, and is sparingly soluble, even on boiling, in water, alcohol, or light petroleum; it crystallises from acetic anhydride in stout, prismatic needles melting at  $248-250^{\circ}$ , and sublimes unchanged. When dissolved in benzene and treated with aniline, a white solid separates, which crystallises from alcohol in glistening, flattened needles melting with decomposition at  $266-267^{\circ}$ . This substance may be the anilic acid, although it was found to contain more than the calculated amount of nitrogen (Found,  $\text{N} = 3.6$  and  $4.0$ . Calculated 3 per cent.).

The author's thanks are due to the Research Fund Committee of the Chemical Society for a grant, which has in part defrayed the cost of this investigation.

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### XXXV.—*A Microscopical Method of Determining Molecular Weights.*

By GEORGE BARGER, Scholar of King's College, Cambridge.

THIS research, a preliminary account of which has been given in the Proceedings (1903, 19, 121), originated in Professor Errera's laboratory at Brussels, where experiments were being carried out on the hereditary adaptation of fungi to strong salt solutions. The fungi were grown in hanging drops of the solutions; each drop was suspended from the lower surface of a coverslip, which was separated from the slide by a cardboard frame, the chamber thus produced being

moistened from time to time with distilled water. The experiments generally lasted a few weeks, and it was noticed that the drops of the salt solutions invariably increased in size. This phenomenon was explained by Prof. Errera in the following manner. As the vapour pressure of the salt solutions was less than that of pure water at the same temperature, and as the drop was confined in a closed space, moistened by pure water, a condensation of vapour took place on the drop. Prof. Errera then asked me to study the effect quantitatively, and for this suggestion and for the kindly interest he has taken in the work I wish to express my hearty thanks. My earliest experiments were made either with small flasks or with small crystallising dishes, which could be completely closed by ground glass plates, but as the results were only of a qualitative character, I finally determined to study the behaviour of the drops in a capillary tube, so that their change in thickness could be measured under the microscope.

#### *Description of the Method.*

A solution of known strength of the substance, the molecular weight of which is unknown, is compared with standard solutions of a substance of known molecular weight, a series of drops taken alternately from the two solutions being introduced into a capillary tube (length 6—8 cm.; bore 1.5 mm.).

After the drops have been measured, the tube is put aside for some time varying from a few minutes to a day, and then another measurement is taken. If there is a decided difference in the vapour pressure of the two solutions employed, one series of drops will be found to have increased, while those alternating with them have decreased. In that case we can decide whether the solution experimented with contains more or less molecules than the standard solution, and so arrive at two limits for the unknown molecular weight.

The theory of the determination is very simple. Each drop is placed between two others of a different solution, and can evaporate on either side into a small, closed air-chamber. This chamber is soon saturated with vapour, which can condense freely on the drops. If the vapour pressures of the two solutions are equal, the evaporation will equal the condensation, and there will be no change in volume of the drops. If, on the other hand, the vapour pressures are unequal, there will be a gradient of vapour pressure in the air spaces; some drops will therefore be in contact with an atmosphere the vapour pressure of which is greater than their own. Condensation will take place on these drops and they will increase. The others, alternating with them, will have a vapour pressure greater than that of the adjoining

air spaces ; these drops will evaporate and thus decrease. Hence there is a distillation from the drops of the one series to those of the other series, although all are at the same temperature.

By measurement, we can tell which drops increase, and hence ascertain which solution has the smaller vapour pressure. If the solvent is identical in both cases, and if the solutes are non-volatile, the solution with the smaller vapour pressure will have the greater concentration of molecules and *vice versa*, and thus the determination of the molecular weight is rendered possible.

### *Preparation of Solutions.*

The supply of the substance, the molecular weight of which is to be determined may be very limited, but good results have been obtained with as little as 30 milligrams. The substance is weighed out in a minute stoppered bottle or cylinder. A known volume of the solvent is then added from a pipette, for instance, a one c.c. pipette graduated in hundredths. It is generally easier to add enough of the solvent to dissolve the substance completely and then weigh the solution. To obtain the volume of the solution, we must know its density, but as the solution is generally dilute, we may, without great error, take its density as being equal to that of the pure solvent. The density of the solvent is easily estimated by a hydrometer.

It is best to express the concentration of the solution thus prepared by volume, and not by weight, as it is easier to make up the other (standard) solutions by volume.

The choice of the standard substance is determined by the following circumstances :

1. In the first place, it should neither be associated nor dissociated under the conditions of the experiment, that is to say, it should actually have the molecular weight deduced from its formula.

2. Secondly, the standard substance must neither combine with the solvent, nor with the other solute (for a certain amount of mixing of the two solutions is inevitable).

3. Thirdly, both the standard and the unknown substance should be very much less volatile than the solvent employed.

4. Fourthly, if the unknown substance is colourless, it is useful to employ a coloured substance as standard, for then one can always see at a glance to which solution a given drop belongs, and to what extent mixing has taken place.

Benzil and azobenzene are two good substances for work with organic liquids. They can be easily obtained pure, are freely soluble in most solvents, have normal molecular weights, and give coloured solutions.

With water, I have most frequently used cane sugar and boric acid. The latter substance has the advantage of not being attacked by moulds, so that its solutions can easily be kept unchanged; its electrolytic dissociation is so slight as to be negligible. The standard solutions are conveniently made up in 10 c.c. graduated stoppered measuring cylinders. It is then easy to obtain a solution of any desired intermediate strength by mixing two others. Sometimes it may be desirable to dilute a solution of known strength very slightly with the pure solvent. In that case, to the known volume of the solution the calculated quantity of the solvent from a one c.c. pipette graduated in hundredths can be added, this procedure being much more accurate than taking the difference between the two readings of the measuring cylinder.

With regard to choice of solvent, the method allows considerable latitude. The solvent need have neither a constant melting point nor a constant boiling point. Therefore, its purity is not an essential condition. Ether saturated with water, wet acetone (b. p. 56.7—65°) alcohol with 10 per cent. water, acetic acid with 20 per cent. water, can all be used successfully.

Boiling point determinations with acetone and pyridine, for instance, require specially purified samples of these substances, whereas by the microscopic method an approximate value of the molecular weight can easily be found in a short time. The best proof that a solvent of constant boiling point is not required is given by the experiments with light petroleum (b. p. 50—60°; see below).

Although the solvent need not be pure, it is obviously essential that all the solutions for one determination should be made up from the same sample. Very volatile solvents cannot be used, for with them it is impossible to fill tubes with any degree of accuracy. I have performed a few experiments with ether and obtained satisfactory results, but cannot recommend this solvent on account of the difficulty of manipulation. With a little care, carbon disulphide may be employed. If, on the other hand, the solvent is not sufficiently volatile, the experiment takes too long. Xylene is one of the least volatile solvents which can conveniently be used.

The *capillary tubes* are best prepared by drawing out soft glass tubing of  $\frac{1}{2}$ " bore into capillaries of 1—2 feet long, which should be cut into smaller pieces, having a smooth, regular edge, in order that the tube may be closed tightly with the finger while it is being filled. The internal diameter of the capillaries should be between 1 and 2 mm., preferably about 1.5 mm. The influence of the bore will be discussed later.

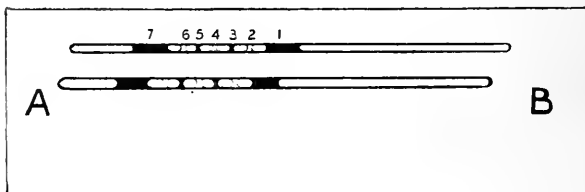
The *filling of the tubes* requires a little practice, but when this has been obtained it can be done quite rapidly. The tube is taken between

the middle finger and thumb, and its upper end, which should be rounded, is closed with the index finger. The other end is then dipped below the surface of one of the two solutions (which in the following experiments is always the standard one). By lifting the index finger very slightly, enough liquid is admitted into the tube to make a column of about 5 mm. long. The index finger is again pressed against the tube, so as to close it, and the tube is then held in a slanting position, with the open end uppermost. By again diminishing the pressure of the finger on the closed end, some air is allowed to escape, and the column of liquid slides down the tube. Its progress is regulated by the amount of slant given to the tube. When the column has travelled about 3 mm., it is stopped by closing the tube again with the finger. The tube is now once more held vertically, and its open end is made to touch the surface of the second solution, while the upper end is still closed by the index finger. This time only a minute drop enters, for the capillary forces are soon balanced by the increase in the pressure of the air inside the tube. The tube is then again held in a slanting position, and the small drop allowed to slide down a short distance, and so on.

Most organic solvents wet the glass and slide down the tube with ease, but with water, especially in narrow tubes, the drop descends very slowly or not at all. This difficulty can be overcome by previously wetting the tube with the first solution to be employed. The drops can also be sucked into the tube by heating the free end and then closing it with the finger. The air, on cooling, contracts, and the drop is forced in.

For the sake of uniformity, I always use tubes with 7 drops; when sealed, the tubes have the following appearance (natural size):

FIG. 1.



*A* is the end which has been dipped in the various solutions.

*B* is the end which is closed by the finger.

In the diagram, the drops are numbered in the order in which they have entered the tube, and the drops of the standard solution are shaded black. The first and last drops are about 5 mm. long, and are not measured, for they generally decrease by evaporation

into the air-spaces at *A* and *B*. They are also the ones most liable to become heated while sealing the tube; for this reason, they are made rather large, in order that their concentration may not so easily be changed by evaporation. The drops 2, 4, and 6 contain the substance the molecular weight of which is being determined.

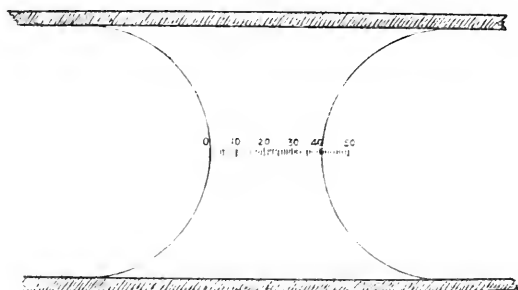
To ensure a rapid interchange of vapour with small differences of concentration, the drops should be close together—say 2 or 3 millimetres apart—but they must not be too close, or they will mix. The thickness of the drops 2—6 is limited by the size of the micrometer scale. Thicker drops can be measured with a lower objective, but then the measurements are, of course, less accurate. With a little practice, drops of the right thickness can easily be obtained. Water gives some difficulty on account of its high surface tension. If too much liquid has been sucked up, the excess can always be removed by means of filter paper. With some heavy liquids in wide tubes, the capillary rise is not great enough, in which case the end of the tube is dipped well under the surface of the liquid, and the pressure of the finger on the other end is slightly diminished until the right quantity of liquid has entered. The same procedure is sometimes necessary with very volatile solvents, the vapour of which may expand by the warmth of the hand, and so tend to drive out drops which have already entered.

When all the drops are in the tube, they are allowed to slide down until the last drop is about 1 cm. distant from the end *A*, and then this end is sealed carefully in the lower part of a small Bunsen flame, and withdrawn immediately. With volatile solvents (acetone, carbon disulphide, &c.), it is advisable to let the last drop get more than 1 cm. from the end *A* before sealing, but there is an objection to letting the drops slide so far down the tube, as will be seen later. Tubes with volatile liquids are best closed by means of soft paraffin wax, at least at the end *A*. A plug of the wax is introduced, and then, by gently warming the end of the tube, it is melted, so as to become air-tight on solidification. The end *B* may be closed by ordinary sealing, or by warming it and letting it suck up a little melted wax while cooling. The wax constitutes a slight source of error, because it attracts some of the solvent from the terminal drops, especially if the experiment lasts a long time. As these end drops are, however, especially long, no great change in their concentration need be feared. Instead of paraffin wax, fusible metal may be used, preferably d'Arcet's alloy with mercury, which melts at 45°. The difficulty here is in getting the alloy into the ends of the tube, owing to the negative capillarity of metals. It can perhaps best be accomplished by means of another thinner capillary, which is dipped into the melted alloy, and then, with some of the metal adhering, it is used to plug up the larger tube.

After the tubes have been filled, the drops are measured. For ease in handling and for purposes of identification, they are fixed to a microscope slide (3" by 1") by means of thick Canada balsam. Each slide is numbered and can take at least half a dozen tubes. The slides are placed in a glass Petri dish about  $3\frac{1}{2}$ " square, and enough water is placed in the dish to cover the tubes, so that the drops are always at the same temperature, and do not move owing to the expansion of the air between them.

Under the microscope, the drops and scale present the following appearance :

FIG. 2.



A sharp image is obtained if the microscope is focussed to the level of the centre of the tube. The menisci then become exceedingly distinct, and the distance between them (which is the minimum thickness of the drop) can be measured. The Petri dish is moved till one of the menisci almost coincides with the zero of the scale; a drop of water between the stage and the dish allows the latter to be moved small distances without jerking. The exact coincidence of the meniscus with the zero is obtained by moving the eye-piece (with the scale in it) transversely in the tube of the microscope, in which it has a little play. As we are only concerned with the *direction* of the change in the drops, not with its *magnitude*, the scale need not be standardised. The distance between the menisci can now be read off to tenths of a scale division. As the micrometer has 50 divisions, 5 numbers below 500 are obtained for each tube. I use a  $\frac{3}{4}$ " objective (Leitz, No. 3); with a lower one, larger drops can be measured on the scale, but the accuracy is correspondingly decreased. With higher objectives, the drops have to be inconveniently small, and the focussing also becomes difficult. The eye-piece should be a strong one, in order to magnify the scale as much as possible. I use a Leitz No. 4 eye-piece; a Zeiss micrometer disc is placed on its diaphragm. With a No. 3 objective, the magnification is about 65 diameters, so that a scale division is equivalent to  $17\ \mu$ , and an accuracy of  $3\ \mu$  is easily obtained.

The time during which the tubes have to be kept before a definite result is obtained varies greatly with the nature of the solvent, the difference in concentration of the solutions, &c.

The changes in the various drops of the same tube are by no means regular. Sometimes all the drops increase if the difference in concentration between them is small. The reason for this is that in filling the tube some of the solution adheres to its walls. This solution forms a dew of minute, convex drops, whereas the large drops, which are measured, have a concave surface. Now, other things being equal, the vapour pressure of a convex surface is greater than that of a concave one (Lehmann: *Molecularphysik*, vol. ii, p. 151). Hence the general tendency of the drops is to increase, and this limits the sensitiveness of the method. If the difference in concentration between the two solutions employed is not very small, the drops of one solution increase much more than those of the other solution, and often, if the tube be kept long enough, the drops which increase least will afterwards decrease.

This initial increase of all drops and subsequent decrease of some is illustrated by the following tube: azobenzene (0.19 mol.) and ethyl benzoate (0.20 mol.) in benzene:

Time.	Readings in tenths of scale divisions.				
12.15 p.m. ....	321	264	289	279	215
2.15 p.m. ....	325	272	292	297	214
5.30 p.m. ....	321	289	286	310	210

As already mentioned, solvents with very high boiling points cannot be used, because the change in the drops occurs too slowly. Theoretically, there is no good reason why tubes should not be kept for an indefinitely long time, so that even the smallest difference of vapour pressure might be demonstrated. In practice, I find, however, that when the difference between the two solutions is small, or when the solvent is insufficiently volatile, the changes in the drops are irregular.

The possibility of keeping tubes at temperatures other than the ordinary naturally suggests itself in this connection. I hoped by this means to apply the method to all high boiling solvents, but my experiments so far have not been successful. The difficulty arises from the necessity of cooling the tubes again before measuring. By cooling, the air spaces between the drops become super-saturated, and the solvent is condensed on the walls of the tube, which, being on the outside, are coldest. Hence, generally, all the drops are smaller than before they were heated.

If the tubes have not been heated too much and if they have been

cooled slowly (for instance, immersed in a large water-bath), good results may nevertheless be obtained. I have kept tubes with water or with acetic acid at a temperature of  $37^{\circ}$ , and in this way the change in the drops is more rapid than at the ordinary temperature. The temperature of the determination can therefore be varied within certain limits ; possibly this may be of use in studying the change of molecular weight with the temperature, for example, of substances which undergo association.

### *Consideration of the Probable Errors.*

The effect of the various manipulations on the accuracy of the method will now be considered. Solutions can be prepared, the concentration of which is accurately known. The only difficulty arises when the supply of the substance is very limited. Through frequent use, the concentration of a solution may gradually undergo a change, for while a tube is being filled, the bottle containing the solution is left open. If the solvent is volatile, it may evaporate ; if hygroscopic, it may attract water from the air ; in the first case, the vapour pressure of the solution will always be lowered ; in the second case, it will only be lowered with low boiling solvents (acetone, alcohol).

If accuracy is desired, it is advisable, after an approximate value has been found, to repeat the last steps in the determination with freshly prepared solutions.

The error due to increased concentration of the solution can be overcome by weighing the residue left on evaporating a small quantity of the solution. This is most easily done with volatile solvents, where it is at the same time of most importance. For the ordinary determinations in this paper, no such special precautions were taken, and the same standard solutions generally served for all the work with a given solvent. The principal object was to find a short and easy method of wide application, not necessarily a very accurate one.

The errors produced in filling the capillaries are as follows. Each drop remains for a moment at the end of the tube before it slides down and is placed between the drops of the other liquid. During this short time, it is exposed to the same influences as the solutions in an open bottle. It may evaporate and absorb moisture ; it presents a relatively large surface to the air, and so may change its vapour pressure. The time of exposure is, however, very short, and may be made approximately equal for the drops of both solutions. The two errors will then balance each other, as we are only concerned with the difference between the two solutions.

Some experiments were performed to study this source of error,

choosing acetone as solvent, because it is both volatile and hygroscopic.

Normal tube, both series of drops composed of benzil in acetone, 0.10 mole,\* and all exposed for 2—3 seconds.

3.21 p.m. ....	347	310	346	283	491
3.37 p.m. ....	351	312	345	290	490
4.3 p.m. ....	357	318	342	298	492

A similar tube, but with the 2nd, 4th, and 6th drops exposed for 10 seconds (the 1st and 7th drops were not measured).

	+	-	+	-	+
3.21 p.m. ....	349	401	366	330	388
3.37 p.m. ....	353	400	371	331	391
4.3 p.m. ....	367	392	382	326	396

It will be seen that whereas the first tube gives no clear result (theoretically, the drops ought not to change at all), the second tube shows that those drops which were exposed for 10 seconds have become distinctly more concentrated than the others.

To get an idea of the amount of concentration, two different solutions of benzil in acetone (strengths 0.09 and 0.10 mole.) were next used.

1. Normal tube, 0.10 benzil as standard (that is, drops 1, 3, 5, 7).

	-	+	-	+	-
11.59 a.m. ....	422	509	491	414	478
12.09 p.m. ....	420	510	488	416	476
12.57 p.m. ....	416	520	478	421	471

2. A similar tube with drops of 0.09 mole. exposed for 5 seconds.

	-	+	-	+	-
1.6 p.m. ....	346	392	331	394	328
1.16 p.m. ....	346	396	331	400	324
1.55 p.m. ....	342	402	330	412	336

3. Same as above, but drops of 0.09 mole. exposed for 10 seconds.

	-	+	-	+	-
11.59 a.m. ....	251	236	246	217	241
12.10 p.m. ....	250	240	250	220	246
12.57 p.m. ....	251	250	248	222	250

\* Throughout this paper the term "mole." signifies a concentration of one gram-molecule per litre.

4. Same as before, but drops of 0.09 mole. exposed for 15 seconds.

1.6 p.m. ....	249	341	222	269	165
1.16 p.m. ....	253	341	224	269	176
1.55 p.m. ....	258	349	225	275	193

From these experiments, it would appear that by an exposure of a quarter of a minute a change of something like 10 per cent. is produced in the concentration of an acetone drop, for only the last tube of the series does not clearly indicate which solution is the stronger. As this time is far in excess of the ordinary differences which occur in filling a tube, the error can only be a slight one. At the same time, it may be one of the reasons for the occasional irregular behaviour of drops in the tube. Sometimes (when the difference between the two solutions is small) there is no regular alternation of increase and decrease, so that no conclusion can be drawn. In that case, the experiment must be repeated.

We now come to the chief interference with the concentration of the drops, namely, their *mixing* with one another. Each drop, as it slides down the tube, leaves a portion of itself behind on the walls. This is shown (in a dry tube) by the decrease of the first drop. The succeeding ones travel over a part which has already been wetted, so they retain their original thickness. As each drop is composed of a different solution from its predecessor, it becomes to some extent mixed with the other solution. That this is so can be easily shown by alternately using a colourless and a coloured solution. For instance, with a potassium permanganate solution and pure water all the drops become pink or red, and the only difference between them is in the intensity of their colour. By making the drops slide up and down the tube a number of times, the mixing becomes more complete, and the difference in their colour disappears.

At first sight, this might seem to be a fatal objection to the method, but such, however, is not the case. The mixing which takes place lessens the difference in concentration between the two series of drops. It cannot, however, obliterate this difference, still less produce a difference in the opposite direction, and the method is only concerned with the *direction* of the difference, not with its *absolute magnitude*. To return to the permanganate solution and water: the drops which were originally composed of pure water will become dilute permanganate solutions; they can never be more concentrated than the other original permanganate drops. Even if an infinite amount of water were added to one drop of permanganate, the resulting mixture would never be pure water.

A difference must, therefore, always remain, and it must remain on

the same side as between the original solutions employed; if we can observe any regular changes in the drops, we shall be able to conclude which solution has the greater vapour pressure.

Although the mixing of the drops does not impair the reliability of the method, it makes it less sensitive. The rate of change depends on the difference between the concentration of the drops, and this difference is decreased by mixing. The mixing should therefore be reduced to a minimum, and it may be useful to consider what conditions will tend to make it so.

Firstly, the amount of liquid which adheres to the walls of the tube varies with the nature of the solution, and seems to depend on its viscosity as well as on its surface tension.

Secondly, the amount of mixing depends on the diameter of the tube. Suppose this diameter to be  $2r$  and the average thickness of the film of liquid which adheres to the walls of the tubes to be  $\delta$  (depending on the nature of the liquid), then, if the drop travel along the tube for a distance  $l$ , it will have lost  $2\pi r\delta l$  (supposing  $\delta$  to be small compared with  $r$ ). If the average thickness of the drop be  $d$ , its volume will be  $\pi r^2 d$ . The proportional loss will be  $\frac{2\pi r\delta l}{\pi r^2 d} = \frac{2\delta l}{rd}$ , and this will approximately represent the amount of mixing. In order to reduce this to a minimum,  $l$  should be small,  $d$  and  $r$  should be large;  $\delta$  is presumably a constant for a given liquid.

1.  $l$  should be small; this means that the drops should slide along as short a piece of the tube as possible.

The distances of each drop from the end of the tube by which it was admitted should be a minimum; the drops must, therefore, be close together, yet not so close that they come into contact and mix. The end drop must be near the entrance of the tube, yet not too close lest it becomes heated when the tube is sealed.

2. The thickness of the drop should be the greatest which can still be measured on the micrometer scale (except in the case of the first and last drops).

3. The tube should be fairly wide, yet sufficiently narrow to allow of the formation of stable drops by surface tension.

It is easy to show that the above general conditions are correct by comparing the behaviour of a coloured and a colourless solution in tubes of widely different bore. Iodine in chloroform and pure chloroform were used for this purpose. The extent of the mixing is indicated by the difference in shade of the two solutions after they have been made to slide up and down the tube a number of times. The difference between the drops sooner becomes imperceptible in the narrow capillary than in the wide one. In the same way, the influence of  $l$  and of  $d$  can be shown.

There is yet another reason why the drops should be close together; their proximity favours the rapid interchange of vapour. This may be inferred from the experiments of Stefan (*Sitzungsber. Wiener Akad.*, 1873, 68, 385) on the rate of evaporation in vertical capillaries. The rate is inversely proportional to the distance of the liquid surface in the tube to the mouth of the tube, and a similar law probably applies to the drops.

It may be asked whether the thin film of liquid which adheres to the walls of the tube does not constitute a permanent means of communication between neighbouring drops. In practice, no such interchange was ever detected (unless the drops actually touch each other). This is probably because the thin layer of liquid sticking to the side of the tube soon breaks up into a number of convex drops, which tend to disappear (as the vapour tension of a convex surface is greater than that of a concave one). Oily liquids which wet the glass with difficulty (ethylene dibromide, aniline) do not leave a uniform film adhering to the walls of the tubes, but a few relatively large drops, which makes it less convenient to work with these liquids.

The next possible source of error is in the closing of the tube. In most cases, the simplest plan is to seal it by holding the end in the lower part of a Bunsen flame. The flame should be steady and the tube should be removed from it as soon as it is completely sealed. The drops nearest the flame are liable to become slightly heated by this process, but the heating only lasts a very short time, so that no appreciable effect can be observed. With liquids such as ether and carbon disulphide and with chloroform (which seems to attack the glass), I prefer to close the tube with melted paraffin wax. In these cases, the heating effect is negligible, but a different error is introduced, because the paraffin wax attracts the organic solvent from the end drop and so gradually concentrates the latter. The end drop is, however, very large, in order that its concentration should only change slowly, whereas with volatile solvents, the change in the measured drops takes place very quickly, before the error due to the paraffin has time to make itself felt. The large size of the end drop is, of course, also useful in counteracting the error due to heating.

Occasionally the tube may turn out to be imperfectly closed; this is at once detected when the tube is measured under water by the movement of the drops and the entrance of the water. In that case, another tube had better be prepared.

In handling the tubes, they must not be jerked or dropped, for this produces sudden and irregular changes in the drops. If the tube is inconveniently long, it must not be scratched with a file, but a piece can be drawn off in a Bunsen flame.

The last error to be considered is the change in the shape of the

drops. The method presupposes that any change in the least diameter (that is, the distance measured) is accompanied by a corresponding change in the volume of the drop. Hence the curvature of the meniscus must remain the same.

This is invariably the case with nearly all organic solvents, but occasionally with water and some less volatile liquids the curvature changes, especially on one side of the drop and if the tube is not quite clean. It does not necessarily follow that the apparent change in the drops is in opposite direction to the real one, but they may become quite out of proportion. This change in the curvature of the meniscus is of rare occurrence and need only be considered with a few solvents; it can, moreover, be readily detected.

#### *Attempted Improvements and Applications of the Method.*

As was said in a previous section, the method only depends on knowing the direction of change in the drops (whether increase or decrease), not the amount of this change. Theoretically, if all the conditions were known, it should be possible to calculate the amount of this change, or, conversely, calculate at once from any observed change the difference in molecular concentration between the drops. It should, moreover, be possible to find the concentration of the unknown solution by interpolation, knowing its behaviour to two known solutions.

A good deal of time was spent in experimenting in this direction, with scarcely any result. The chief aim was to know the influence of the difference in concentration of the drops on their rate of change, the other conditions being kept constant.

To eliminate the variations in the diameter, pieces of thermometer tubing of uniform bore were used. The drops were placed at approximately equal distances from one another. All the solutions contained the same solute, and differed only in strength. The temperature was kept constant, and a special method of filling the tubes with capillary syringes was used in order to prevent mixing. The tubes were closed with wax.

Another attempt to study the change in the drops quantitatively was to use capillary tubes of about 6—10 mm. long, which were slightly constricted in the middle, so that they would, at this point, retain by capillarity a measured drop of a solution. These tubes were put horizontally into a Petri dish filled with distilled water without being sealed. In this way, mixing was excluded, as in the previous plan. These experiments did not even show a constant rate of change when all the known conditions were constant. The only

general statements which can be made about this rate of change in the drops is that it increases with the temperature, with the difference in concentration and with the proximity of the drops, and that the influence of the diameter of the tube is doubtful.

There are a few special problems which might perhaps be solved by the present method, such as the ionisation of salts in mixtures of an ionising with a non-ionising solvent. Similarly, the method may be used in studying association in mixtures of associative and a non-associative solvent (for example, alcohol and benzene). Some preliminary experiments on this are given at the end of the paper.

So far, I have mainly devoted myself to showing that the new method is reliable, widely applicable, and sufficiently accurate to be of real practical use in organic chemistry.

### *Results.*

The value of a new quantitative method can only be proved by the results obtained with it; a large number of determinations with various solvents have therefore been made.

In the experimental records, I have not only mentioned in each case the strength of the two standard solutions—the one hypertonic, the other hypotonic to the unknown solution—but the actual changes which were observed in the drops are also given. In this way, the personal factor has been eliminated.

In order to illustrate the degree of sensitiveness, and by way of showing the accuracy obtainable in the micrometer readings, some measurements are first given with different urea solutions in 90 per cent. alcohol.

#### *I. Odd drops 0.095 mole.; even drops 0.10 mole.*

Concentration	0.095	0.10	0.095	0.10	0.095	0.10	0.095	0.10	0.095
Apr. 7, 11 a.m.	312	340	384	76	376	448	417	361	128
12 a.m.	312	340	378	82	369	448	413	360	126
1 p.m.	312	342	376	86	368	449	413	361	126
2 p.m.	311	344	372	92	362	449	413	361	125
3 p.m.	310	345	372	96	360	451	413	362	126
4 p.m.	308	346	370	100	358	450	412	362	128
5 p.m.	306	346	367	102	358	450	410	360	126
6 p.m.	304	348	366	105	356	450	408	361	130
Apr. 8, 10 a.m.	272	342	363	114	356	452	402	368	149

II. *Odd drops 0.10 mole. ; even drops 0.095 mole.*

Concentration	0.10	0.095	0.10	0.095	0.10	0.095	0.10	0.095	0.10
Apr. 7, 11 a.m.	233	255	189	240	248	256	240	270	262
12 a.m.	235	253	190	236	248	256	239	267	261
1 p.m.	235	252	194	236	250	257	239	268	261
2 p.m.	335	250	195	234	250	258	239	265	263
3 p.m.	233	250	197	232	250	260	240	264	265
4 p.m.	232	250	199	232	251	261	240	262	266
5 p.m.	230	248	201	231	252	262	240	261	264
6 p.m.	230	247	202	230	252	262	240	261	265
Apr. 8, 10 a.m.	206	232	202	228	256	268	242	262	285

III. *Odd drops 0.24 mole. ; even drops 0.25 mole.*

Concentration	0.24	0.25	0.24	0.25	0.24	0.25	0.24	0.25	0.24
Apr. 3, 1 p.m.	73	360	364	347	384	367	345	371	379
2.30 p.m.	75	367	356	342	382	368	341	372	372
4 p.m.	75	372	353	350	380	369	340	374	372
5.30 p.m.	73	375	351	354	377	367	336	373	365
Apr. 4, 10 a.m.	77	373	345	361	385	370	333	378	364
Apr. 6, 10 a.m.	36	344	325	358	408	354	342	382	372

The changes in the drops of the foregoing three tubes are very slight, yet they are so regular as to show the great accuracy of the measurements. The tables illustrate a further point: the drops on the right hand side, that is, those which have travelled furthest up the tube and have the greatest chance of becoming mixed, show, generally, a smaller rate of change than the other drops on the left. For this reason, I have confined myself to five measured drops. The first and the last drop in each tube, as seen in the preceding tables, do not behave in a regular manner. Therefore, the five above-mentioned drops were enclosed between two large ones which were not measured.

To economise space, in all further cases the *change* in the drops is alone recorded, not their actual measurement. For the same reason, the changes for those standard solutions which were most nearly isotonic with the unknown solution are alone given. By way of example, other concentrations of the standard solution have been included in the case of the first two determinations (glucose and mannitol in water). With these exceptions, therefore, only those tubes have been included which have the slowest rate of change. All the other tubes gave results more quickly on account of the greater difference between the two solutions contained in them.

*Water.**Glucose*, 25.02 grams per litre (0.139 mole.).

Cane sugar	0.05 mole.	18 hours	+230	-97	+71	-79	+71	+548
"	"	0.10 "	18 "	+26	-18	+25	-31	+130
"	"	0.12 "	21 "	+6	-4	+9	-4	+27
		46 "	+21	-22	+13	-10	+15	
"	"	0.13 "	3 "	+3	+1	+8	0	+2
		22 "	+8	+3	+5	-1	+5	+16
		70 "	+18	+4	+15	-1	+10	
"	"	0.14 "	22 "	-1	0	-2	+2	-7
"	"	0.15 "	18 "	-3	+8	0	+9	-24
"	"	0.20 "	18 "	-41	+55	-57	+53	-251
"	"	0.25 "	25 mins.	-3	+2	+1	+3	+1
		18 hours	-75	+85	-81	+65	-78	-384

In the above and all subsequent tables of measurements, the first column gives the concentration of the standard solution, the second that of the time from the beginning of the experiment (where several times are given with one concentration, these times all apply to the same tube). The next column gives the changes observed during that time in five drops. The figures denote tenths of a micrometer scale division. As has already been said in the description of the method, the first, third, and fifth of these drops contain the substance the molecular weight of which is being determined (glucose in this case). The other two are composed of the standard solution, and in addition the whole series of five are enclosed between two large drops of the standard solution which are not measured. In the last column is shown the change between the aggregate thickness of the three glucose drops and that of the two cane sugar drops (in a period of about 20 hours). These figures show at once that the glucose solution is somewhere between 0.13 and 0.14 mole. They also show that the rate of change in the drops is greatly influenced by the difference between their concentrations.

Assuming the molecular weight of cane sugar to be 342, we have now for glucose  $M$  between  $\frac{25.02}{0.14}$  and  $\frac{25.02}{0.13}$ .

$M$  between 179—192. Mean 186;  $C_6H_{12}O_6$  requires 180.

*Mannitol*, 15·69 grams per litre (0·0862 mole.).

Cane sugar	0·064 mole.	24 hours	+5	-7	+4	-7	+10	+33
"	"	0·072 "	24 "	+4	-4	+3	-2	+3
"	"	48 "	+7	-5	+5	-5	+10	+16
"	"	0·080 "	24 "	0	-1	0	+1	+1
"	"	48 "	+2	-1	+1	+3	0	+1
"	"	0·088 "	24 "	-2	+5	-1	+3	-4
"	"	48 "	-1	+3	-1	+4	-1	-15
"	"	0·096 "	24 "	-2	+12	-7	+4	-5
"	"							-30

The mannitol solution is practically isotonic with the cane sugar of 0·080 mole.

$$M = \frac{15\cdot69}{0\cdot08} = 196; \text{C}_6\text{H}_{14}\text{O}_6 \text{ requires } 182.$$

*Mannitol*, 11·41 grams per litre (0·063 mole.).

Cane sugar	0·056 mole.	8 hours	+1	+1	+1	+3	-2
"	"	24 "	-2	+4	-3	+6	-6
"	"	0·060 "	8 "	+1	-1	+2	+2
"	"	24 "	0	-1	+1	-1	+2

Molecular weight of mannitol = 190—204, mean 197;  $\text{C}_6\text{H}_{14}\text{O}_6$  requires 182.

*Boric Acid as Standard.*

*Cane sugar*, 95·76 grams per litre (0·28 mole.).

Boric acid	0·30 mole.	22 hours	0	-13	+12	-15	+12
"	"	0·29 "	17 "	-5	+14	-4	+8
"	"						+1

Molecular weight of cane sugar = 319—331, mean 325;  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$  requires 342.

In the foregoing and following calculations, no allowance has been made for the electrolytic dissociation of boric acid, but if ionisation is considered, then the result for cane sugar approaches more nearly to the theoretical value.

*Urea*, 12·00 grams per litre (0·20 mole.).

Boric acid	0·195 mole.	15 hours	+9	-5	+7	-11	+24
"	"	0·20 "	21 "	-1	+7	-1	+5
"	"						+1

Molecular weight of urea = 60—61·5;  $\text{CH}_4\text{ON}_2$  requires 60.

*Tartaric Acid*, 30.00 grams per litre (0.20 mole.).

Boric acid	0.19 mole.	21 hours	+3	-1	+8	-2	+5
"	"	0.20 "	21 "	+4	+4	+3	+4
		45 "	+4	+13	+9	+6	+19
(other tube)	0.20 "	96 "	+10	+8	+8	-2	-1
	0.21 "	21 "	-6	+19	-3	+3	0

Molecular weight = 143—157;  $C_4H_6O_6$  requires 150.

*Succinic Acid*, 18.29 grams per litre (0.155 mole.).

Boric acid	0.15 mole.	23 hours	+4	-4	+10	-15	-18
"	"	0.16 "	24 "	+2	+17	-1	+12

Molecular weight = 114—122;  $C_4H_6O_4$  requires 118.

*Mannitol*, 29.12 grams per litre (0.16 mole.).

Boric acid	0.165 mole.	22 hours	+10	-7	+9	-10	+11
"	"	0.17 "	18 "	-5	+8	-2	-4

Molecular weight = 166—171;  $C_6H_{14}O_6$  requires 182.

*Catechol*, 15.95 grams per litre (0.145 mole.).

Boric acid	0.13 mole.	15 hours	+22	-9	+18	-5	0
"	"	0.14 "	23 "	-20	+19	-3	+30

Molecular weight = 114—123;  $C_6H_6O_2$  requires 110.

*Glucose*, 28.8 grams per litre (0.16 mole.).

Boric acid	0.17 mole.	18 hours	+14	-40	+33	-27	+38
"	"	0.175 "	21 "	-1	+3	-2	+1

Molecular weight = 165—170;  $C_6H_{12}O_6$  requires 180.

The following two determinations show electrolytic dissociation:

*Potassium Nitrate*, 10.1 grams per litre (0.10 mole.).

Boric acid	0.19 mole.	21 hours	+11	-18	+8	+1	+2
"	"	0.195 "	21 "	-1	+11	-31	0

$i$  (van't Hoff's coefficient) = 1.92.

*Sodium Chloride*, 5.85 grams per litre (0.10 mole.).

Boric acid	0.17 mole.	21 hours	+10	-3	+10	-10	+18
"	"	0.175 "	24 "	+1	+1	-5	0
"	"	0.18 "	45 "	0	+13	+1	+18

Taking the salt to be isotonic with 0.175 mole.,  $i = 1.75$ .

*Tryptophan.* For a specimen of this substance, I have to thank Dr. F. G. Hopkins of Cambridge (*J. Physiol.*, 1903, 29, 451).

Boric acid	0·075 mole.	1 day	+19	-1	+10	-1	+4
Cane sugar	0·085 „	2 days	+3	+19	+1	+10	-11

Two c.c. of the solution left, on evaporation, 0·0368 gram of tryptophan.

$$M = \frac{0\cdot0368}{0\cdot002 \times 0\cdot08} = 230 ; C_{11}H_{12}O_2N_2 \text{ requires } 204.$$

*Alcohol.*

The experiments were performed either with commercial "absolute" alcohol (99·5 per cent.), or with 90 per cent. methylated spirits.

*α-Naphthol as Standard; 99·5 per cent. Alcohol.*

*Azobenzene*, 30·94 grams per litre (0·17 mole.).

α-Naphthol	0·16 mole.	100 mins.	+13	-13	+20	-11	+15
„	0·18 „	125 „	-26	+21	-30	+32	-18

Molecular weight = 172—193 ;  $C_{12}H_{10}O_2$  requires 182.

*Phenyl Salicylate*, 38·52 grams per litre (0·18 mole.).

α-Naphthol	0·17 mole.	50 mins.	+1	-3	+4	-3	+1
„	0·19 „	90 „	-17	+14	-2	+5	-8

Molecular weight = 203—227 ;  $C_{13}H_{10}O_3$  requires 214.

*Salicylic Acid*, 24·84 grams per litre (0·18 mole.).

α-Naphthol	0·17 mole.	45 mins.	+5	-3	+5	-1	+2
„	0·19 „	90 „	-10	+10	-12	+12	-14

Molecular weight = 131—146 ;  $C_7H_6O_3$  requires 138.

*Benzoic Acid*, 21·96 grams per litre (0·18 mole.).

α-Naphthol	0·17 mole.	30 mins.	+3	-1	+2	-1	+4
„	0·19 „	90 „	-7	+4	-7	+1	-1

Molecular weight = 115—129 ;  $C_7H_6O_2$  requires 122.

*Catechol*, 19·80 grams per litre (0·18 mole.).

α-Naphthol	0·17 mole.	45 mins.	+5	-4	+3	-3	+4
„	0·19 „	80 „	-3	+5	0	+9	-3

Molecular weight = 104—116 ;  $C_6H_6O_2$  requires 110.

*Resorcinol*, 19.80 grams per litre (0.18 mole.).

$\alpha$ -Naphthol	0.17 mole.	80 mins.	+11	-9	+11	-3	+6
„	0.19 „	80 „	-10	+23	-22	+16	0

Molecular weight = 104—116 ;  $C_6H_6O_2$  requires 110.

*Quinol*, 19.80 grams per litre (0.18 mole.).

$\alpha$ -Naphthol	0.17 mole.	45 mins.	+4	-3	+11	-5	+6
„	0.19 „	80 „	-2	+7	-1	+6	0

Molecular weight = 104—116 ;  $C_6H_6O_2$  requires 110.

*Cinnamic Acid*, 26.64 grams per litre (0.18 mole.).

$\alpha$ -Naphthol	0.17 mole.	30 mins.	0	-5	+13	-9	+3
„	0.19 „	30 „	-2	-3	-5	-2	-8
		15 hours	-24	+40	-32	+37	-30

Molecular weight = 140—157 ;  $C_9H_8O_2$  requires 148.

*Acetanilide*, 24.30 grams per litre (0.18 mole.).

$\alpha$ -Naphthol	0.17 mole.	90 mins.	+4	0	+8	-4	+5
„	0.19 „	110 „	-8	+20	-17	+31	-19

Molecular weight = 128—143 ;  $C_8H_9ON$  requires 135.

*Diphenylamine*, 30.42 grams per litre (0.18 mole.).

$\alpha$ -Naphthol	0.17 mole.	60 mins.	+11	-7	+13	-9	+8
„	0.19 „	125 „	0	+7	-7	+6	+1

Molecular weight = 160—178 ;  $C_{12}H_{11}N$  requires 169.

The error in the preceding ten determinations in no case exceeds 5 per cent., but a greater deviation from the theoretical value was found with the following substances: hippuric acid, diphenyl, dinitrobenzene, and urea. These all gave values which were more than 10 per cent. too high as compared with  $\alpha$ -naphthol in absolute alcohol.

It was repeatedly found that the molecular weight of urea was too high as compared with other substances. Urea is therefore not a good standard. This is further illustrated by the first of the following three determinations, all of which were carried out in 90 per cent. of methylated spirit.

*Urea as Standard ; 90 per cent. Alcohol.**Phenyl Salicylate*, 38.52 grams per litre (0.18 mole.).

Urea 0.18 mole.	20 hours	0	-6	+12	-10	+18
„ 0.19 „	2 „	-2	+2	0	0	-3
„ 0.20 „	2 „	-2	+6	-1	+5	-7

The change with 0.19 mole. is not very decisive. The phenyl salicylate solution gives values between 0.18 and 0.20 mole. (probably between 0.18 and 0.19). Taking the values 0.18 and 0.20, we get :

Molecular weight = 193—214 ;  $C_{13}H_{10}O_3$  requires 213.

*Phenyl Salicylate as Standard ; 90 per cent. Alcohol.**Azobenzene*, 29.12 grams per litre (0.16 mole.).

Phenyl salicylate 0.15 mole.	130 mins.	+8	-3	+21	+2	+5
„ 0.16 „	90 „	-13	+23	-13	+7	-27

Molecular weight of azobenzene = 182—194 ;  $C_{12}H_{10}N_2$  requires 182.

*Benzil*, 23.10 grams per litre (0.11 mole.).

Phenyl salicylate 0.115 mole.	70 mins.	+20	-19	+18	-40	-1
„ 0.12 „	120 „	-6	+7	-10	+6	-5

Molecular weight of benzil = 193—201 ;  $C_{14}H_{10}O_2$  requires 210.

*Acetone.*

The acetone used for all the experiments contained water and boiled between 56.7° and 65°. Various substances were used as standard.

*With Phenyl Salicylate as Standard.**Salicylic Acid*, 27.40 grams per litre.

Phenyl salicylate 0.18 mole.	35 mins.	+12	-10	+15	-26	+31
„ 0.19 „	20 „	-7	+7	-10	+12	-1

Molecular weight = 124—131, mean 127 ;  $C_7H_6O_3$  requires 138.

*Picric Acid*, 45.80 grams per litre.

Phenyl salicylate 0.20 mole.	11 mins.	+11	-7	+8	-11	+17
„ 0.21 „	48 „	-3	0	-6	+5	-14

Molecular weight = 217—229, mean 223 ;  $C_6H_3O_7N_3$  requires 229.

*Benzil*, 42.00 grams per litre.

Phenyl salicylate	0.20 mole.	22 mins.	+54	-76	+93	-71	+75
,,	0.21	,, 15	-8	+71	-67	+88	-47

Molecular weight = 200—210, mean 205 ;  $C_{14}H_{10}O_2$  requires 210.

*Phenol*, 18.8 grams per litre.

Phenyl salicylate	0.17 mole.	40 mins.	+6	0	+6	-2	+6
,,	0.18	,, 30	-8	+24	-22	+29	-14

Molecular weight = 103—111, mean 107 ;  $C_6H_6O$  requires 94.

*With Salicylic Acid as Standard.*

*Phenol*, 18.8 grams per litre.

Salicylic acid	0.16 mole.	20 mins.	+48	-12	+3	-2	+11
,,	0.17	,, 20	-21	+75	-48	+27	-21

Molecular weight = 111—119, mean 115 ;  $C_6H_6O$  requires 94.

The two values for phenol are a good deal too high. This is because the vapour pressure of phenol is not negligible at the ordinary temperature. To further illustrate this point, I made some determinations with aniline as standard. Although two substances having approximately the same boiling point need not have nearly the same vapour pressure at the ordinary temperature, yet the boiling point gives a general indication as to the volatility of the substance.

*With Aniline as Standard.*

*Phenol*, 18.8 grams per litre.

Aniline	0.19 mole.	80 mins.	+22	-3	+16	-19	0
,,	0.20	,, 120	-4	+14	+1	+5	-14

Molecular weight = 94—99, mean 97 ;  $C_6H_6O$  requires 94.

*Nitrobenzene*, 24.6 grams per litre.

Aniline	0.19 mole.	25 mins.	+2	-5	+16	-15	+2
,,	0.20	,, 25	-13	+1	-13	+17	-21

Molecular weight = 117—123, mean 120 ;  $C_6H_5O_2N$  requires 123.

*Ethyl Benzoate*, 30.00 grams per litre.

Aniline 0.19 mole.	50 mins.	+30	-2	+7	-11	+10
„ 0.20 „	20 „	-5	0	-5	+2	-5

Molecular weight = 143—150, mean 146;  $C_9H_{10}O_2$  requires 150.

The last three determinations give good results. The boiling points of phenol, nitrobenzene, and ethyl benzoate are close to that of aniline. With the same standard, the molecular weight of a considerably less volatile substance is found to be too low.

*Phenyl Salicylate*, 38.52 grams per litre (0.18 mole.).

Aniline 0.21 mole.	60 mins.	0	-30	+70	-92	+175
„ 0.22 „	—	-6	+12	-7	+2	-11

Molecular weight = 175—182, mean 178;  $C_{13}H_{10}O_3$  requires 214.

In the same way, the molecular weights of salicylic acid and of catechol are found to be more than 10 per cent. too low when these substances are compared with aniline. Conversely, for camphor and phenetole, which are more volatile, values are found which are a good deal too high.

As a last example of a determination in acetone solution, I give that of a new substance kindly given me by Dr. Ruhemann (Trans., 1903, 84, 1133).

*Dimethoxybisketocoumaran*.

Owing to the small quantity available (0.04 gram) the process was slightly modified. The strength of the solution of the substance was determined after it had been rendered isotonic with a solution of benzil.

1.0415 grams of the solution left a residue of 0.0315 gram of the substance. The density of the acetone was 0.794; hence the volume of this solution was 1.312 c.c. and the solution contained 24.01 grams per litre.

The following readings were obtained :

With benzil, 0.0775 mole.	23 mins.	+9	-7	+31	-19	+19
„ 0.080 „	30 „	0	+4	0	+4	-3
„ 0.0825 „	13 „	-4	+13	-3	+7	-8

The solution of the new substance was therefore between 0.0775 and 0.080 mole.

Taking 0.0775 as the value, we get  $M = \frac{24.01}{0.0775} = 309$ .  $C_{18}H_{14}O_6$  requires 326.

*Acetic Acid.*

Glacial acetic acid was used, with benzil as standard substance.

*Acetanilide*, 18.90 grams per litre (0.14 mole.).

Benzil	0.135 mole.	23 hours	+45	-68	+95	-105	+160
„	0.145 „	23 „	-10	+36	-20	+12	-89

Molecular weight = 130—138, mean 134;  $C_8H_9ON$  requires 135.

*Triphenylmethane*, 34.16 grams per litre (0.14 mole.).

Benzil	0.135 mole.	45 hours	0	-9	+2	-3	+5
„	0.145 „	21 „	-58	+30	-30	+29	-31

Molecular weight = 236—253, mean 245;  $C_{19}H_{16}$  requires 244.

*Picric Acid*, 27.48 grams per litre (0.12 mole.).

Benzil	0.115 mole.	19 hours	+10	-4	+23	-6	+7
„	0.12 „	19 „	-16	+21	-31	+37	-10

Molecular weight = 229—239, mean 234;  $C_6H_3O_7N_3$  requires 229.

*Diphenyl*, 21.56 grams per litre (0.14 mole.).

Benzil	0.10 mole.	17 hours	+10	-4	+23	-6	+7
„	0.11 „	21 „	-16	+21	-31	+37	-10

Molecular weight = 196—216, mean 206;  $C_{12}H_{10}$  requires 154.

The last of these determinations was repeated, but the same high value was found, this inaccuracy differing markedly from the exact results obtained in the three preceding examples.

The following is an example of a determination in a mixed solvent namely, 80 per cent. acetic acid, 20 per cent. water:

*Acetanilide*, 29.83 grams per litre.

Urea	0.20 mole.	17 hours	+6	+1	+12	-3	+5
„	0.208 „	17 „	-4	+24	-6	+8	-1

Molecular weight = 143—147, mean 145;  $C_8H_9ON$  requires 135.

*Benzene.*

In all the experiments except the last, azobenzene was used as standard substance; in this case, it was benzil.

*Benzil*, 42·00 grams per litre (0·20 mole.).

Azobenzene	0·19 mole.	4 hours	+ 4	- 9	- 2	- 6	+ 7
„	0·21 „	30 mins.	- 13	+ 5	- 8	+ 11	- 3

Molecular weight = 200—221;  $C_{14}H_{10}O_2$  requires 210.

*Diphenyl*, 30·80 grams per litre (0·20 mole.).

Azobenzene	0·19 mole.	100 mins.	+ 7	- 2	+ 5	+ 3	+ 10
„	0·20 „	18 hours	- 32	+ 11	- 20	- 2	- 13

Molecular weight = 154—162, mean 158;  $C_{12}H_{10}$  requires 154.

*Triphenylmethane*, 48·80 grams per litre (0·20 mole.).

Azobenzene	0·20 mole.	30 mins.	+ 4	- 10	0	0	+ 3
„	0·215 „	3 hours	- 2	+ 9	- 8	+ 4	- 2

Molecular weight = 227—244, mean 235;  $C_{19}H_{16}$  requires 244.

*Diphenylamine*, 33·80 grams per litre (0·20 mole.).

Azobenzene	0·19 mole.	100 mins.	+ 3	0	+ 4	+ 1	+ 4
„	0·21 „	100 „	- 1	+ 6	- 4	+ 3	0

(With 0·20 mole., no definite result could be obtained.)

Molecular weight = 161—177;  $C_{12}H_{11}N$  requires 169.

*$\alpha$ -Nitronaphthalene*, 34·60 grams per litre (0·20 mole.).

Azobenzene	0·18 mole.	75 mins.	+ 9	- 7	+ 1	- 3	+ 1
„	0·20 „	5 hours	- 10	- 2	- 13	+ 8	- 12

(With 0·19 mole., no definite result could be obtained.)

Molecular weight = 173—192, mean 183;  $C_{10}H_7O_2N$  requires 173.

*m-Dinitrobenzene*, 32·26 grams per litre (0·192 mole.).

Azobenzene	0·18 mole.	75 mins.	+ 7	0	- 2	- 4	+ 6
„	0·19 „	2 hours	+ 1	0	- 21	+ 3	- 4

Molecular weight = 170—179, mean 175;  $C_6H_4O_4N_2$  requires 168.

*Ethyl Benzoate*, 30·00 grams per litre (0·20 mole.).

Azobenzene	0·18 mole.	70 mins.	+ 16	0	+ 5	- 2	+ 7
„	0·19 „	5 hours	0	+ 25	- 3	+ 31	- 5

Molecular weight = 158—167, mean 162;  $C_9H_{10}O_2$  requires 150.

Ethyl benzoate is slightly volatile; phenetole is still more so, and accordingly gives a higher molecular weight.

*Phenetole*, 23.42 grams per litre (0.192 mole.).

Azobenzene	0.16 mole.	40 mins.	+12	-1	+5	+1	+12
„	0.17 „	150 „	-9	+16	-1	+40	-14

Molecular weight = 138—146, mean 142;  $C_8H_{10}O$  requires 122.

*Triphenylguanidine*, 28.70 grams per litre (0.10 mole.).

Azobenzene	0.09 mole.	65 mins.	+53	-2	+8	-8	+1
„	0.10 „	130 „	-7	+9	-1	+6	-3

Molecular weight = 287—319, mean 303;  $C_{19}H_{17}N_3$  requires 287.

The following acids show association in benzene solution :

*Benzoic Acid*, 24.40 grams per litre (0.20 mole.).

Azobenzene	0.10 mole.	85 mins.	+6	-3	+3	-1	+2
„	0.11 „	70 „	0	+6	-4	+1	0

Molecular weight = 222—244, mean 233;  $C_7H_6O_2$  requires 122.

*Cinnamic Acid*, 29.60 grams per litre (0.20 mole.).

Azobenzene	0.17 mole.	45 mins.	-31	+27	-22	+20	-27
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The change in the drops is a large one in a small time.

The molecular weight is considerably above 174;  $C_9H_8O_2$  requires 148.

*Azobenzene*, 20.02 grams per litre (0.11 mole.).

Benzil	0.10 mole.	4 hours	+12	-44	+18	+5	+17
„	0.12 „	4 „	-15	+13	+2	+22	-1

Molecular weight of azobenzene = 167—200;  $C_{12}H_{10}N_2$  requires 182.

### *Chloroform.*

With chloroform, there was often some difficulty in sealing the tubes; the glass was attacked, and did not fall together very easily. Hence paraffin wax was always used to close the capillaries.

*Phenyl Salicylate as Standard.*

*Benzil*, 42.00 grams per litre (0.20 mole.).

Phenyl salicylate	0.19 mole.	2 hours	+16	-19	+30	-23	+52
„	0.21 „	2 „	-11	+4	-8	+4	-2

Molecular weight = 200—220;  $C_7H_{10}O_2$  requires 210.

*m*-Dinitrobenzene, 33·60 grams per litre (0·20 mole.).

Phenyl salicylate	0·21 mole.	2 hours	+19	-6	+3	-6	+14
„	0·22 „	3 „	-4	+3	-7	+18	-21

Molecular weight = 153—160 ;  $C_6H_4O_4N_2$  requires 168.

*Benzil as Standard.*

*Triphenylmethane*, 24·40 grams per litre (0·10 mole.).

Benzil	0·095 mole.	2 hours	+19	-6	+3	-6	+14
„	0·105 „	3 „	-4	+3	-7	+18	-21

Molecular weight = 232—256 ;  $C_{19}H_{16}$  requires 244.

*Diphenyl*, 15·40 grams per litre (0·10 mole.).

Benzil	0·095 mole.	1 hour	+4	-8	+1	-6	+2
„	0·105 „	1 „	-6	+2	-4	+4	-1

Molecular weight = 146—162 ;  $C_{12}H_{10}$  requires 154.

*Diphenylamine*, 16·90 grams per litre (0·10 mole.).

Benzil	0·09 mole.	10 mins.	+7	+1	+7	+2	+7
„	0·095 „	2 hours	-5	+3	-1	+3	-3

Molecular weight = 178—188 ;  $C_{12}H_{11}N$  requires 169.

*m*-Dinitrobenzene, 16·80 grams per litre (0·10 mole.).

Benzil	0·09 mole.	2 hours	+31	-22	+16	0	+37
„	0·095 „	3 „	-2	+14	-3	+11	-1

Molecular weight = 177—187 ;  $C_6H_4O_4N_2$  requires 168.

*Phenyl Salicylate*, 21·40 grams per litre (0·10 mole.).

Benzil	0·09 mole.	40 mins.	+3	-2	+6	-3	+8
„	0·095 „	2 hours	-8	+5	-1	+6	-5

Molecular weight = 225—238 ;  $C_{13}H_{10}O_3$  requires 214.

$\alpha$ -Nitronaphthalene, 17·30 grams per litre (0·10 mole.).

Benzil	0·09 mole.	90 mins.	+15	-1	+3	0	+6
„	0·10 „	—	-12	+9	-5	+6	-7
„	0·095 „	(gave no distinct result)					

Molecular weight = 173—192 ;  $C_{10}H_7O_2N$  requires 173.

*Caffeine* (anhydrous, dried at  $110^{\circ}$ ), 19.4 grams per litre (0.10 mole.).

Benzil	0.10	mole.	3 hours	+10	-9	+4	-6	+10
„	0.105	„	1 hour	-8	+4	-2	+6	-7

Molecular weight = 185—194;  $C_8H_{10}O_2N_4$  requires 194.

*Caffeine* (with water of crystallisation), 21.2 grams per litre (0.10 mole.).

Benzil	0.105	mole.	2 hours	+6	-4	+28	-12	+28
„	0.11	„	2 „	-3	+4	-1	+2	-1

Molecular weight = 193—202;  $C_8H_{10}O_2N_4 \cdot H_2O$  requires 212.

*Cocaine* (crystalline, dried at  $110^{\circ}$ ), 30.3 grams per litre (0.10 mole.).

Benzil	0.105	mole.	50 mins.	+2	-22	+13	-17	+17
„	0.11	„	—	-6	+9	-6	+5	-10

Molecular weight = 275—289;  $C_{17}H_{21}O_4N$  requires 303.

*Piperine* (air-dried crystals), 28.5 grams per litre (0.10 mole.).

Benzil	0.105	mole.	45 mins.	+14	-8	+16	-2	+2
„	0.11	„	100 „	-2	+10	-5	+4	-4

Molecular weight = 259—271;  $C_{17}H_{19}O_3N$  requires 285.

*Quinine* (precipitated, dried at  $120^{\circ}$ ), 32.4 grams per litre (0.10 mole.).

Benzil	0.09	mole.	50 mins.	+5	-3	+6	-5	+20
„	0.095	„	2 hours	-24	+27	-20	+30	-22

Molecular weight = 341—360;  $C_{20}H_{24}O_2N_2$  requires 324.

### *Phenylbenzylmethylethylammonium Iodide.*

For a specimen of this salt, I am indebted to Mr. H. O. Jones (Trans., 1903, 83, 1419). Two determinations were made.

#### *I. Triphenylmethane as Standard.*

0.0487 gram of the iodide was dissolved in 2 c.c. of chloroform, this being equivalent to 24.35 grams per litre.

Afterwards 2.358 grams of the solution left 0.0370 gram of salt, dried at  $70^{\circ}$ . Density of chloroform = 1.502.

This gives a concentration of  $\frac{37 \times 1.502}{2.358} = 23.6$  grams per litre. Mean concentration = 23.9 grams per litre.

Triphenylmethane	0.07 mole.	30 mins.	+22	-11	+20	-22	+42
„	0.075 „	70 „	+4	+4	+2	+5	+9
„	0.08 „	30 „	-5	+4	-3	+3	-3

Taking the concentration to be 0.075 mole. :  $M = \frac{23.9}{0.075} = 319$ .

## II. Azobenzene as Standard.

0.2008 gram of salt in 8 c.c. = 25.1 grams per litre.

Azobenzene	0.07 mole.	35 mins.	+15	-10	+4	0	+3
„	0.075 „	23 „	-3	+2	-1	0	-5

Mean = 0.725 mole.

$$M = \frac{25.1}{0.0725} = 346 ; \text{C}_{16}\text{H}_{20}\text{NI requires } 353.$$

*α-Phenylbenzylmethylallylammonium Iodide*.—This salt, for a sample of which I am indebted to Mr. H. O. Jones, is of special interest because Wedekind, its discoverer, has recently found that by the ebullioscopic method its molecular weight is one-third of the normal value (*Zeit. physikal. Chem.*, 1903, 46, 235).

## Triphenylmethane as Standard.

0.2771 gram of salt in 4.70 c.c. = 59.0 grams per litre (0.162 mole. theoretically).

Triphenylmethane	0.17 mole.	—	-16	+13	-8	+9	-6
„	0.15 „	70 min.	-1	+9	-3	+3	-4

This was within a few hours of making up the iodide solution. The molecular weight of the salt is greater than the normal value. Next morning, the determination was continued :

Triphenylmethane	0.15 mole.	20 mins.	+6	-1	+3	-2	+5
„	0.17 „	15 „	-1	+4	-1	+5	-5
„	0.155 „	1 hour	+10	-4	+3	-5	+15

Taking the numbers 0.155 and 0.17 (intermediate concentrations giving uncertain results), it was found that the values for the molecular weight ranged between 335 and 381 (mean 358);  $\text{C}_{17}\text{H}_{20}\text{NI}$  requires 365.

A second determination was made.

0.5450 gram of salt in 7.60 c.c. of chloroform = 71.71 grams per litre (0.196 mole.).

Within 2 hours of making up this solution :

Triphenylmethane	0.150 mole.	—	+8	-2	+14	-28	+26
„	0.165 „	35 mins.	-23	+20	-23	+9	-12

Molecular weight = 435—478, mean 457.

The salt is therefore associated, as in the previous determination. The new solution (71.71 grams per litre) was now directly compared with the old one (59.0 grams per litre), which had been made some days previously.

The old solution as standard	7 mins.	-8	+9	-5	+10	-11
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The new solution contains, therefore, less molecules. Two days later this had changed :

The old solution as standard	95 mins.	+10	-5	+5	-6	+34
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The molecular weight in the new solution had diminished. The following numbers were obtained :

Triphenylmethane	0.21 mole.	7 mins.	-8	0	-2	+7	-2
„	0.238 „	15 „	+18	-1	+2	-1	+21

Molecular weight between 301 and 341, mean 321.

The effect of heat was next tried. The second iodide solution was divided into two parts, one of which was kept overnight at the ordinary temperature, the other at 37°, both in tightly stoppered bottles in the dark. The determinations were made on the following day, the solution which had not been heated being taken as standard :

30 mins.	+22	-16	+17	-9	+15
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The molecular concentration of the solution has been, therefore, considerably increased by heating. This explains the fall in the molecular weight observed by Wedekind in employing the ebullioscopic method.

#### *Carbon Disulphide.*

Triphenylmethane was used as standard. The other substances were used in solutions of 0.20 mole.

*Azobenzene*, 36.4 grams per litre.

Standard	0.19 mole.	15 mins.	+13	-14	+14	-17	+6
„	0.20 „	100 „	-26	-2	-28	+5	-2

Molecular weight = 182—192, mean 187 ;  $C_{12}H_{10}N_2$  requires 182.

*Diphenyl*, 30·8 grams per litre.

Standard	0·20 mole.	35 mins.	+3	+1	+4	0	+8
„	0·21 „	45 „	-7	+3	-12	0	-32

Molecular weight = 147—154, mean 150;  $C_{12}H_{10}$  requires 154.

*Phenyl Salicylate*, 42·8 grams per litre.

Standard	0·18 mole.	50 mins.	+2	-7	-4	-8	+1
„	0·19 „	—	-15	-11	-19	+6	-30

Molecular weight = 225—238, mean 232;  $C_{13}H_{10}O_3$  requires 214.

*$\alpha$ -Nitronaphthalene*, 34·6 grams per litre.

Standard	0·18 mole.	—	+5	-1	0	+4	+10
„	0·19 „	15 mins.	-18	-2	-30	+7	-16

Molecular weight = 172—192, mean 182;  $C_{10}H_7O_2N$  requires 173.

*Ethyl Benzoate*, 30·0 grams per litre.

Standard	0·19 mole.	25 mins.	+2	-7	0	-12	+2
„	0·20 „	35 „	-14	+17	-6	-1	-7

Molecular weight = 150—158, mean 154;  $C_9H_{10}O_2$  requires 150.

*Phenetole*, 24·4 grams per litre.

Standard	0·18 mole.	15 mins.	+9	-3	+5	-1	+3
„	0·19 „	35 „	-16	+1	-1	+17	0

Molecular weight = 128—136, mean 132;  $C_8H_{10}O$  requires 122.

The behaviour of the last two substances is interesting, since ethyl benzoate is very slightly volatile, and phenetole rather more so. In benzene, for instance, solutions of 0·20 mole. behave as if they were respectively between 0·18 and 0·19 mole. and between 0·16 and 0·17 mole. Carbon disulphide is much more volatile than benzene, so ethyl benzoate and phenetole approach more nearly to the theoretical values. As the latter substance is the more volatile of the two, it gives a greater difference from the theory than the former.

*Benzoic Acid*, 24·4 grams per litre.

Standard	0·10 mole.	30 mins.	+45	-77	+60	-40	+37
„	0·11 „	—	-8	+9	-4	+8	0

Molecular weight = 222—244, mean 233;  $C_7H_6O_2$  requires 122.

*Phenol*, 18.4 grams per litre.

Standard 0.10 mole.	—	+5	+1	+5	+1	+4
„ 0.11 „	12 mins.	-1	+5	-1	+1	-2

Molecular weight = 167—184, mean 180;  $C_6H_6O$  requires 94.

It will be seen that, while ethyl benzoate and phenetole give normal values, the substances with which they are closely connected, namely, benzoic acid and phenol, have almost double the normal molecular weight. This association was to be expected in a non-hydroxylic solvent like carbon disulphide. When the hydrogen of the hydroxyl is replaced by ethyl, the association disappears.

*Sulphur*.

The determination of the molecular weight of sulphur in carbon disulphide gave the following numbers:

Triphenylmethane, 0.14 mole.	14 mins.	+4	-8	+6	-20	+5
„ 0.15 „	35 „	-1	+18	0	+5	-2

After these results had been obtained, the strengths of the standard solutions were checked. Of the solution called 0.15 mole., 5 c.c. left on evaporation 0.2030 gram of triphenylmethane. Its concentration had, therefore, changed during the determination to 0.166 mole., and the other solution, obtained from it by dilution, was in reality 0.155 mole. The mean = 0.160 mole. may be taken to represent the strength of the sulphur solution.

Of this, 1.70 c.c. left on evaporation 0.0738 gram of sulphur, that is, 43.4 grams per litre.

1.00 c.c. left on evaporation 0.0432 grams of sulphur, that is, 43.2 grams per litre.

Mean, 43.3 grams per litre. 0.160 gram-molecules = 43.3.

Molecular weight of sulphur = 270 =  $S_8 - S_9$ .

This is in close agreement with the value previously obtained by E. Beckmann (*Zeit. physikal. Chem.*, 1890, 5, 8) who finds as an average  $S_8 = 256$ .

*Light Petroleum*.

A fraction boiling between 50° and 60° was obtained from ordinary light petroleum by distilling once with a Young's still-head. All the substances were tried at a concentration of 0.10 mole., on account of the sparing solubility of certain of them. Azobenzene was used as standard in all cases.

*Triphenylmethane*, 24·4 grams per litre.

Azobenzene	0·10 mole.	40 mins.	+5	-1	+1	-6	+3
„	0·108 „	25 „	+1	+9	+1	+11	-6

Molecular weight = 226—244, mean 235 ;  $C_{19}H_{16}$  requires 244.

*Diphenyl*, 15·4 grams per litre.

Azobenzene	0·09 mole.	14 mins.	+8	+1	+4	0	+5
„	0·10 „	150 „	-10	+14	-21	+30	+3

Molecular weight = 154—169, mean 162 ;  $C_{12}H_{10}$  requires 154.

*Diphenylamine*, 16·9 grams per litre.

Azobenzene	0·09 mole.	100 mins.	+2	-15	+59	-29	+36
„	0·10 „	40 „	-1	+7	-8	+26	+6

Molecular weight = 169—186, mean 178 ;  $C_{12}H_{11}N$  requires 169.

*Phenyl Salicylate*, 21·4 grams per litre.

Azobenzene	0·10 mole.	40 mins.	+5	-1	+1	-6	+3
„	0·108 „	—	+1	+10	+4	+10	0

Molecular weight = 198—214, mean 206 ;  $C_{13}H_{10}O_3$  requires 214.

The above non-volatile substances give quite satisfactory values for their molecular weight, but this is not the case with the following substances, the vapour pressure of which at the ordinary temperature is not negligible.

*Camphor*, 15·2 grams per litre.

Azobenzene	0·07 mole.	15 mins.	+6	-14	+7	-10	+5
„	0·08 „	85 „	-11	+21	-12	+37	-6

Molecular weight = 190—217, mean 203 ;  $C_{10}H_{16}O$  requires 152.

*Naphthalene*, 12·8 grams per litre.

Azobenzene	0·07 mole.	15 mins.	+6	-1	+9	-4	+2
„	0·08 „	130 „	-11	+48	-59	+47	-2

Molecular weight = 160—183, mean 171 ;  $C_{10}H_8$  requires 128.

*Phenetole*, 12·2 grams per litre.

Azobenzene	0·07 mole.	15 mins.	+3	-5	+1	0	0
„	0·08 „	85 „	-9	+58	-47	+30	-13

Molecular weight = 152—174, mean 163 ;  $C_8H_{10}O$  requires 122.

*Ethyl Benzoate*, 15.0 grams per litre.

Azobenzene	0.08 mole.	85 mins.	+29	0	+20	0	+30
,,	0.09	,,	—	-1	+10	-4	+20
							-2

Molecular weight = 167—187, mean 177;  $C_9H_{10}O_2$  requires 150.

As might have been expected, ethyl benzoate gives a result most nearly approaching to the real value, because it is the least volatile of this series. As petroleum is a non-hydroxylic solvent, phenols, acids, &c., are associated in it, and give high values for their molecular weights. This is shown by the following examples:

*Thymol*, 15.0 grams per litre.

Azobenzene	0.07 mole.	30 mins.	+4	-6	+1	-10	-3
,,	0.08	,,	35	,,	-1	+12	-13
						+30	-18

Molecular weight = 188—214, mean 201;  $C_{10}H_{14}O$  requires 150.

*Trichlorophenol*, 19.7 grams per litre.

Azobenzene	0.07 mole.	35 mins.	+15	+2	+25	+3	+20
,,	0.08	,,	35	,,	-1	+9	-3
						+27	-3

Molecular weight = 246—281, mean 263;  $C_6H_3OCl_3$  requires 197.

*Pyridine*.

The pyridine, which was a commercial specimen containing a little water, boiled at 115—118°. Benzil and azobenzene were used as standard substances. Of the other substances, solutions of 0.20 mole. were prepared.

*Diphenylamine*, 33.8 grams per litre.

Benzil	0.19 mole.	90 mins.	+4	0	+1	0	+1
,,	0.20	,,	5 hours	-2	+1	-1	+1
							-3

Molecular weight = 169—178; mean 174;  $C_{12}H_{11}N$  requires 169.

*Cinnamic Acid*, 29.6 grams per litre.

Benzil	0.19 mole.	17 hours	+20	-28	+26	-10	+31
,,	0.20	,,	95 mins.	-1	+2	-11	+20
							-8

Molecular weight = 148—156, mean 152;  $C_9H_8O_2$  requires 148.

*Salicylic Acid*, 27.6 grams per litre.

Benzil	0.19 mole.	7 hours	+8	-1	+4	-20	+30
,,	0.21 ,	7 ,	-3	+8	+1	+5	+1

Molecular weight = 131—145, mean 138 ;  $C_7H_6O_3$  requires 138.

*Triphenylmethane*, 48.8 grams per litre.

Benzil	0.18 mole.	20 hours	+28	-12	+12	-6	+22
,,	0.19 ,	2 ,	-10	+27	-26	+34	-25

Molecular weight = 257—271, mean 264 ;  $C_{19}H_{16}$  requires 244.

*Azobenzene*, 36.4 grams per litre.

Benzil	0.18 mole.	20 hours	+16	-21	+10	-19	+15
,,	0.19 ,	16 ,	-20	+38	-127	+130	-13

Molecular weight = 192—202, mean 197 ;  $C_{12}H_{10}N_2$  requires 182.

*Acetanilide*, 27.0 grams per litre.

Benzil	0.18 mole.	5 hours	+3	-7	+2	-5	+2
,,	0.19 ,	16 ,	-21	+9	-9	+17	0

Molecular weight = 142—150, mean 146 ;  $C_8H_9ON$  requires 135.

 *$\alpha$ -Nitronaphthalene*, 34.6 grams per litre.

Benzil	0.18 mole.	5 hours	+9	-6	+2	-9	+7
,,	0.19 ,	2 ,	-3	+2	-8	+5	-4

Molecular weight = 182—192, mean 187 ;  $C_{10}H_7O_2N$  requires 173.

 *$\alpha$ -Naphthol*, 28.8 grams per litre.

Benzil	0.21 mole.	22 hours.	+16	-28	+39	-22	+17
,,	0.22 ,	5 ,	-4	+8	-4	+5	0

Molecular weight = 131—136, mean 134 ;  $C_{10}H_8O$  requires 144.

Judging from the comparatively small errors in the values for cinnamic and salicylic acids and for  $\alpha$ -naphthol, the association in pyridine does not seem very marked, which is in accordance with the results obtained by Ross Innes (Trans., 1901, 79, 261).

Abnormal results were obtained for the following : *m*-dinitrobenzene, phenyl salicylate, diphenyl (more than 10 per cent. too high), picric acid, succinic acid, thiocarbanilide (more than 10 per cent. too low).

With azobenzene as standard, the error for *m*-dinitrobenzene and for diphenyl was 5—10 per cent.

*Ether.*

The ether was previously saturated with water to avoid the effect of atmospheric moisture. The tubes were sealed with paraffin wax.

*Diphenyl*, 30.8 gram per litre (0.20 mole.).

Benzil	0.18 mole.	4 mins.	+8	-3	+4	-2	0
„	0.22 „	5 „	0	+5	+1	+8	-2

Molecular weight of diphenyl = 140—171;  $C_{12}H_{10}$  requires 154.

*Quinol*, 22.0 grams per litre (0.20 mole.).

Benzil	0.18 mole.	4 mins.	+5	-3	+2	-2	+26
„	0.22 „	4 „	-10	+1	-3	+5	-4

Molecular weight of quinol = 100—122;  $C_6H_6O_2$  requires 110.

*Xylene.*

*Triphenylmethane*, 51.24 grams per litre (0.21 mole.).

Benzil	0.17 mole.	55 mins.	+15	-6	+1	-3	+1
„	0.223 „	—	-24	+12	-9	+10	-4

Molecular weight of triphenylmethane = 230—301, mean, 265;  $C_{19}H_{16}$  requires 244.

*Association in Mixtures of an Associative and a Non-associative Solvent.*

As the microscopic method is particularly suited for work with mixed solvents, it seems desirable to study with its help the problems of association. The results of some preliminary experiments are here communicated, and although no special attention was paid to accuracy, the values show the general nature of the association in mixtures.

The object in view was to determine the molecular weight of acids, phenols, &c., in mixtures of varying composition of two solvents, the boiling points of which are not very remote, and in one of which the substance has a normal molecular weight, whereas it is associated in the other.

Such pairs of solvents are: ether and carbon disulphide, methyl alcohol and chloroform, ethyl alcohol and benzene, &c. Determinations were carried out with the second and third pairs, using cinnamic and benzoic acids respectively as solutes. In both cases, the concentration

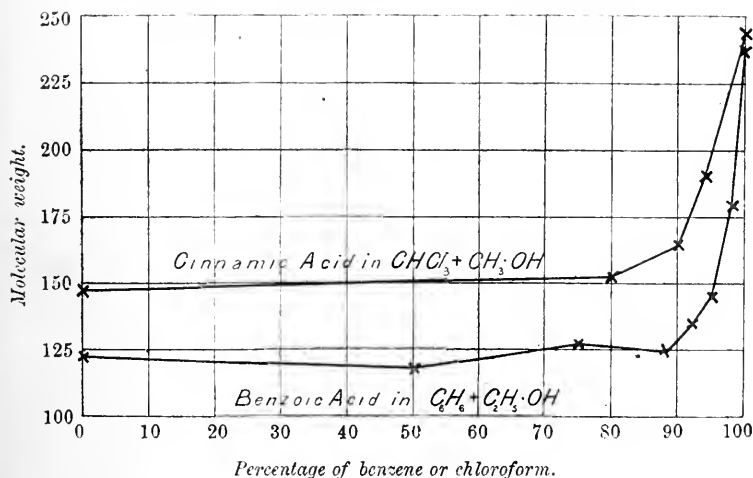
was 0.20 mole., the standard substance was benzil, and the temperature was  $16^{\circ}$ .

Mixtures were made containing the two solvents in known proportion by volume, and with each mixture the cinnamic (or benzoic) acid solution was prepared, together with the necessary benzil solutions.

Benzoic acid in crystallisable benzene and absolute ethyl alcohol;  
24.4 grams per litre.

50 per cent.	f	benzil	0.204 mole.	5 mins.	+4	-2	+1	-1	+7	mean=0.208
benzene	l	,,	0.212	,, 30	,,	-8	-1	-5	+3	M. W.=117
75 per cent.	f	,,	0.19	,, 2 hours	+5	-11	+6	-8	+1	mean=0.192
benzene	l	,,	0.195	,, 1	,,	-2	+6	-2	+3	M. W.=127
87.5 per cent.	f	,,	0.19	,, —	+16	-1	+9	+2	+8	mean=0.196
benzene	l	,,	0.202	,, 4	,,	-39	+41	-3	+9	M. W.=124
92 per cent.	f	,,	0.175	,, 1	,,	+8	-16	+3	-14	mean=0.18
benzene	l	,,	0.185	,, 18	,,	-28	+31	-11	+53	M. W.=136
95 per cent.	f	,,	0.16	,, $\frac{1}{2}$	,,	+1	-5	0	-3	mean=0.17
benzene	l	,,	0.18	,, 1	,,	+1	+3	-1	+4	M. W.=144
98 per cent.	f	,,	0.13	,, —	+9	+3	+7	+4	+11	mean=0.135
benzene	l	,,	0.14	,, —	+3	+10	-5	+14	-5	M. W.=181
100 per cent.	f	,,	0.095	,, 1	,,	+2	-1	+3	0	mean=0.103
benzene	l	,,	0.112	,, 2	,,	-1	+8	0	+7	M. W.=237

Among the results given in an earlier section of this paper there



will be found for the molecular weight of benzoic acid in pure benzene 233, and in alcohol 122, both in concentrations of 0.20 mole,

II. Cinnamic acid : 29.6 grams per litre ; methyl alcohol and chloroform not specially purified.

80 per cent. f benzil	0.19	mole.	50 mins.	+4	-7	+1	-11	+5	mean=0.195
chloroform	0.20	..	12 ..	-7	+1	-3	+1	-2	M. W.=152
90 per cent. f ..	0.175	..	40 ..	+2	-4	0	+1	+3	mean=0.18
chloroform	0.185	..	55 ..	+5	+1	-3	+12	-2	M. W.=164
94 per cent. f ..	0.15	..	8 ..	+2	-2	+2	-3	+4	mean=0.155
chloroform	0.16	..	90 ..	-5	+13	0	+20	+3	M. W.=191
100 per cent. f ..	0.119	..	1 hour	+7	+1	+5	-4	+6	mean=0.122
chloroform	0.125	..	15 mins.	-10	+6	-13	+9	-25	M. W.=243

The molecular weight of cinnamic acid in 100 per cent. methyl alcohol has not been determined, but in ethyl alcohol it was found to be 148.

The values for benzoic acid may be slightly vitiated by its relatively considerable vapour pressure at the ordinary temperature. With the molecular weights as ordinates and the percentage of benzene or chloroform as abscissæ, two curves have been plotted which clearly show that a small proportion of alcohol is sufficient to do away with the association. Should this observation prove to be general, it may be of considerable practical importance in those cases where one is restricted to associative solvents because the substance is not sufficiently soluble in the others. A small percentage of a non-associative solvent would not materially affect the solubility, yet it would reduce the molecular weight to its normal value.

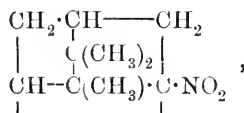
THE WELLCOME PHYSIOLOGICAL RESEARCH LABORATORIES,  
HERNE HILL, S.E.

# XXXVI.—*Studies in the Camphane Series. Part XIII.* *Action of Nitrogen Peroxide on 1-Nitrocamphene*

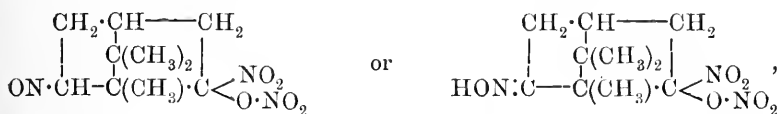
By MARTIN ONSLOW FORSTER and FRANCES MARY GORE MICKLETHWAIT.

IN connection with the study of *isonitrosocamphor*, it seemed probable that an examination of structural isomerides would furnish useful information, and we have therefore attempted to prepare a substance of this class from 1-nitrocamphene, the compound obtained by the action of silver nitrate on 1-bromo-1-nitrocamphane dissolved in alcohol (Forster, *Trans.*, 1901, 79, 644).

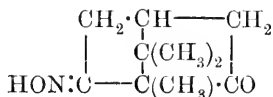
The behaviour of 1-hydroxycamphene towards bromine, which converts it into  $\beta$ -bromocamphor (*Trans.*, 1902, 81, 264), renders it probable that the constitution of 1-nitrocamphene is expressed by the formula



and the fact that this compound readily yields additive derivatives with bromine, hydrogen bromide, and hydrogen iodide led us to hope that nitrogen peroxide would give rise to the nitrosate,



from which on hydrolysis, followed by elimination of nitrous acid, an *isonitrosocamphor* having the constitution



should be formed.

On submitting 1-nitrocamphene to the action of nitrogen peroxide, we obtained a compound having the composition  $\text{C}_{10}\text{H}_{15}\text{O}_6\text{N}_3$ , and therefore containing the elements of  $\text{N}_2\text{O}_4$  in addition to those of the original material. The substance, however, although empirically the nitrosate of 1-nitrocamphene, is not a genuine member of this class, because alcoholic ammonia and piperidine, instead of transforming it into a nitrolamine and a piperidide respectively, convert it into a substance,  $\text{C}_{10}\text{H}_{14}\text{O}_4\text{N}_2$ , identical with the product arising from the limited action of alcoholic potash. Moreover, the high melting point

and sparing solubility of this nitrosate suggest a bimolecular character, but we have no evidence that it belongs to the class of dioxime peroxides. Furthermore, the treatment to which it has been subjected has failed to provide us with the structural isomeride of isonitrosocamphor.

Circumstances having compelled us to interrupt the investigation, and costliness in time and material precluding the likelihood of its being resumed, we confine ourselves to recording the changes which have been observed, without speculating on the constitution of the substances obtained.

*Action of Nitrogen Peroxide on 1-Nitrocamphene.*

The nitrocamphene required for the investigation was prepared by the method already described (Trans., 1901, 79, 646), and on repeating this process 20 or 30 times it was found that when alcoholic silver nitrate acts on 1-bromo-1-nitrocamphane, a certain amount of the silver salt leaves the solution in combination with nitrocamphene. After evaporating off the greater portion of the alcoholic filtrate from the silver bromide, the liquid yielded colourless crystals when left for several hours. This product, when suspended in boiling water, gave a solution of silver nitrate from which highly purified nitrocamphene was obtained by distillation in steam. The circumstances controlling the formation of the substance, however, could not be determined; it was isolated on several occasions, but in more frequent cases the crystalline deposit consisted of the compound of silver nitrate with silver bromide.

The nitrogen peroxide was prepared by heating dry lead nitrate, and was passed into solutions containing 10 grams of nitrocamphene in 50 c.c. of chloroform. The liquid gradually became pale brown, and a rise of temperature occurred; when a considerable amount of gas had been absorbed, the colour became greenish-brown, and at 50° lustrous crystals appeared, and increased rapidly. The passage of the gas was then interrupted, and, after an interval of 12 hours, the intensely green, or bluish-green liquid was filtered. The conditions of this experiment have been considerably varied from time to time with the object of improving the yield, but although the operation has been repeated more than 50 times, we have not succeeded in obtaining the nitrosate in quantities exceeding 24 per cent.

The crude substance is usually stained with blue, which is retained with some persistence. By recrystallisation from boiling alcohol, 100 c.c. of which are required by 1 gram, the substance is obtained in lustrous, snow-white, flattened needles which melt and completely decompose at 217°. The greatest difficulty has been experienced in

obtaining concordant results in the combustion of this compound, owing to the readiness with which nitrous gases are eliminated on heating; whilst the determinations of nitrogen have served to distinguish between the nitrosate and the nitrosite, we cannot claim to have established conclusively the empirical formula  $C_{10}H_{15}O_6N_3$  in preference to  $C_{20}H_{28}O_{12}N_6$ .

0.2262 gave 0.3670  $CO_2$  and 0.1222  $H_2O$ .  $C = 44.25$ ;  $H = 6.05$ .

0.2003 „ 0.3280  $CO_2$  „ 0.1070  $H_2O$ .  $C = 44.67$ ;  $H = 5.98$ .

0.2043 „ 27.4 c.c. nitrogen at  $17^\circ$  and 766 mm.  $N = 15.69$ .

0.1803 „ 23.4 c.c. „ at  $16^\circ$  „ 782 mm.  $N = 15.58$ .

$C_{10}H_{15}O_6N_3$  requires  $C = 43.95$ ;  $H = 5.50$ ;  $N = 15.38$  per cent.

$C_{20}H_{28}O_{12}N_6$  „  $C = 44.11$ ;  $H = 5.01$ ;  $N = 15.44$  „

$C_{10}H_{15}O_5N_3$  „  $C = 46.69$ ;  $H = 5.84$ ;  $N = 16.34$  „

One gram of the nitrosate requires nearly 600 c.c. of cold alcohol to dissolve it, and the compound is very sparingly soluble in all organic media; we have not been able, therefore, to determine its molecular weight, but this behaviour, and a comparison of the temperature at which it decomposes with the melting points of the derivatives herein described, and of 1-nitrocamphene ( $56^\circ$ ), indicate the bimolecular expression,  $C_{20}H_{30}O_{12}N_6$ .

The substance is insoluble in boiling aqueous potassium hydroxide and in hot concentrated hydrochloric acid; it dissolves in fused phenol, and develops an intense green coloration when the solution is warmed gently with concentrated sulphuric acid, but the colour disappears on dilution and is not regenerated by alkalis. In fuming nitric acid, it dissolves slowly, without rise of temperature, and is precipitated unchanged on dilution; concentrated sulphuric acid dissolves it less readily, but on warming gently a clear, deep brown solution is formed, from which gas is slowly evolved.

#### *Action of Piperidine on the Nitrosate.*

Ten grams of the nitrosate were covered with 8 grams of piperidine, when the liquid became hot and the crystals dissolved. Having completed the action by heating for a short time on the water-bath, the viscous product was poured into water, yielding a crystalline solid weighing 6 grams. On recrystallising the substance twice from hot absolute alcohol, it was obtained in transparent, flattened prisms melting at  $123^\circ$ .

0.1988 gave 0.3857  $CO_2$  and 0.1136  $H_2O$ .  $C = 52.90$ ;  $H = 6.39$ .

0.1875 „ 0.3640  $CO_2$  „ 0.1064  $H_2O$ .  $C = 52.94$ ;  $H = 6.35$ .

0.2470 „ 26.8 c.c. nitrogen at  $16^\circ$  and 756 mm.  $N = 12.59$ .

$C_{10}H_{14}O_4N_2$  requires  $C = 53.10$ ;  $H = 6.19$ ;  $N = 12.39$  per cent.

These results show that the product is not a piperidide, but is produced by elimination of the elements of nitrous acid from the foregoing substance. It is insoluble in hot dilute sulphuric acid and in a 10 per cent. solution of potassium hydroxide; it gives no coloration with ferric chloride, is indifferent towards fuming nitric acid, and does not give Liebermann's reaction. Phosphorus pentachloride has no action on it. Boiling petroleum dissolves it very sparingly, and although only moderately soluble in cold alcohol, it dissolves readily in the heated liquid.

A solution containing 0.5920 gram in 25 c.c. of chloroform at  $21^{\circ}$  gave  $\alpha_D - 7^{\circ}32'$  in a 2-dcm. tube, whence  $[\alpha]_D - 159.0^{\circ}$ .

The transformation of the nitrosate into the compound  $C_{10}H_{14}O_4N_2$  can be effected also by the action of alcoholic ammonia, and, under certain conditions, by alcoholic potash. When the former agent is employed, and heated with the nitrosate under a reflux apparatus, the crystals become completely dissolved in about 15 minutes, and the smell of ammonia is then scarcely perceptible; on cooling the liquid, an oil separates and rapidly solidifies. If alcoholic potash is used, it is necessary to limit the quantity of alkali, because the product undergoes further decomposition if an excess is employed.

Ten grams of the nitrosate were suspended in 25 c.c. of hot absolute alcohol and treated with 5 grams of potassium hydroxide in the minimum of water. After five minutes on the water-bath, a clear, yellow solution was produced, from which a crystalline precipitate separated on cooling. This was identical with the product obtained by the action of piperidine, and, on evaporating the alcohol from the filtrate, a residue was obtained which dissolved very readily in water; this solution set free iodine from potassium iodide, and yielded a dark green oil when acidified.

Evidence of the elimination of nitrous acid was obtained also in using piperidine. The filtrate from the solid substance precipitated by water was neutralised with dilute sulphuric acid, which precipitated a sticky, blue material; on filtering the liquid, adding alkali, extracting with ether, and evaporating the solvent, an oil was obtained which gave Liebermann's reaction very intensely, and most probably consisted of nitrosopiperidine.

#### *Complete Hydrolysis of the Nitrosate.*

Although the compound  $C_{10}H_{14}O_4N_2$  is obtainable from the nitrosate by the action alike of piperidine, alcoholic ammonia, and alcoholic potash, this fact is only true of the last named when the action is restricted, for if excess of the agent is employed the product is a

potassium derivative which forms a dark brown solution in water and yields a green oil on acidification.

This compound can be separated also as a by-product in the preparation of the nitrosate, for if the chloroform filtrate from that substance is shaken with 10 per cent. potassium hydroxide, the latter becomes brown, and furnishes the green oil on treatment with acid.

Owing to the unstable character of the liquid, we have not been able to determine its composition, but crystalline derivatives have been obtained from it, and are described below. The ethereal solution, when dried with calcium chloride and evaporated, yields a bright green varnish, which turns brown spontaneously and evolves a gas without colour or odour; if a freshly prepared specimen is heated in boiling water, it decomposes suddenly, emitting clouds of brown fumes with considerable violence, and becoming converted into a charred mass. If an attempt is made to distil the green oil in steam the colour changes to brown, but nothing volatile is produced; the brown product, unlike the green substance from which it is obtained, is insoluble in sodium carbonate, but dissolves in caustic alkali. It has not been found possible to obtain crystalline derivatives of the green oil by the action of phenyl isocyanate or of benzoyl chloride. Concentrated hydrochloric acid does not eliminate hydroxylamine, and reduction with sodium amalgam has failed to give a definite product; oxidation with potassium permanganate takes place very readily in the alkaline solution, and appears to decompose the substance completely.

#### *Action of Potassium Ferricyanide on the Green Oil.*

Twenty grams of the nitrosate were suspended in 150 c.c. of absolute alcohol and heated on the water-bath during two hours with 14 grams of caustic potash dissolved in the minimum quantity of water; the alcohol was then evaporated and the residue taken up with water, in which it dissolved completely. To this liquid, which was pale brown, 500 c.c. of a 25 per cent. solution of potassium ferricyanide were added, when a dark brown colour was developed in the liquid, the temperature of which rose to about 40°, whilst slight effervescence occurred. After an interval of 12 hours, dilute sulphuric acid was added until a greenish-blue coloration was produced; the viscous, brown oil which separated was removed and washed several times, when it became solid and was purified by reprecipitation from the solution in sodium carbonate, followed by crystallisation of the dried substance (about 14 grams) from light petroleum.

The same substance has been obtained from nitrocamphene in the following manner. One hundred grams, after treatment with nitrogen

peroxide in the manner described, having furnished 24.2 grams of the nitrosate, the chloroform filtrate was extracted with 300 c.c. of 30 per cent. potassium hydroxide solution, which became dark brown. This liquid was treated with 1200 c.c. of a 25 per cent. solution of potassium ferricyanide, and the mixture, which had evolved gas and risen in temperature, was acidified with dilute sulphuric acid after an interval of 3 hours; the brown oil quickly hardened and was redissolved in sodium carbonate, filtered from a little insoluble tarry matter, and reprecipitated. The pale brown solid obtained in this manner weighed 51.5 grams.

As in the case of the nitrosate, we have encountered difficulties in analysing this substance, which has, we believe, the empirical formula  $C_{10}H_{14}O_5N_2$ .

0.1786 gave 0.3275  $CO_2$  and 0.1067  $H_2O$ .  $C = 50.01$ ;  $H = 6.64$ .

0.1954 „ 19.8 c.c. nitrogen at  $20^\circ$  and 763 mm.  $N = 11.63$ .

$C_{10}H_{14}O_5N_2$  requires  $C = 49.59$ ;  $H = 5.78$ ;  $N = 11.57$  per cent.

It dissolves readily in organic media excepting light petroleum, 1000 c.c. of a boiling concentrated solution in the latter depositing 4.2 grams in the form of snow-white needles melting at  $85-86^\circ$ . It dissolves readily in sodium carbonate forming a pale yellow liquid, and the solution in 2 per cent. sodium hydroxide yields an intense purple-blue precipitate with ferrous sulphate. The alcoholic solution develops with ethereal ferric chloride a red coloration which is not very intense, and on adding copper acetate dissolved in alcohol the deep bluish-green colour of the copper salt changes to grass-green, but no separation of crystals takes place.

The compound does not decolorise bromine dissolved in chloroform, but hydrogen bromide is evolved on boiling the solution. The solution in phenol develops a green coloration when warmed with concentrated sulphuric acid, changing to a very deep bluish-green; on dilution, the colour becomes pink and then changes to intense blue on adding alkali. Fuming nitric acid dissolves the substance without any rise of temperature taking place, and phosphorus pentachloride, nitrous acid, potassium permanganate, benzoyl chloride, alcoholic potash, and boiling acetyl chloride are also without action.

The substance is not affected by hot concentrated hydrochloric acid, and after heating it during 2 hours with alcohol and hydrochloric acid in a sealed tube at  $100^\circ$ , it crystallised from the liquid, and the filtrate did not reduce Fehling's solution even when boiled. Dry hydrogen chloride was passed into a solution of the compound in methyl alcohol during 2 hours without producing a trace of a methyl derivative.

By dissolving it in excess of standardised sodium hydroxide and

titrating with sulphuric acid in presence of phenolphthalein, concordant results have been obtained without difficulty.

0.0861 gram dissolved in 10 c.c. of sodium hydroxide solution (containing 3.926 grams per litre) required 5.7 c.c. of sulphuric acid (containing 4.92 grams per litre), whence 242 grams require 46.0 grams NaOH.

0.1063 gram dissolved in 12 c.c. of sodium hydroxide solution required 6.7 c.c. of sulphuric acid, whence 242 grams require 46.0 grams NaOH.

The *ammonium* derivative separated when the substance was treated with concentrated ammonia, forming colourless needles which became yellow at about  $115^{\circ}$  and decomposed violently at  $136^{\circ}$ ; after remaining during 2 days in the desiccator, the substance did not change colour until heated at about  $140^{\circ}$ ; it decomposed at  $155^{\circ}$ .

0.2045 gave 27.8 c.c. nitrogen at  $18^{\circ}$  and 767 mm.  $N = 15.86$ .

$C_{10}H_{17}O_5N_3$  requires  $N = 16.21$  per cent.

The *copper* derivative crystallised in blue needles on adding copper sulphate to the ammoniacal solution, becoming olive-green after 2 days in the desiccator.

0.2152 gave 0.0208 CuO.  $Cu = 7.72$ .

$(C_{10}H_{13}O_5N_2)_2Cu$ ,  $C_{10}H_{14}O_5N_2$  requires  $Cu = 8.08$  per cent.

The *silver* derivative formed a pale yellow, granular precipitate on adding silver nitrate (1 mol.) to a neutral solution of the ammonium derivative.

0.1326 gave 0.0404 Ag.  $Ag = 30.46$ .

$C_{10}H_{13}O_5N_2Ag$  requires  $Ag = 30.96$  per cent.

It darkens rapidly on exposure to light, and dissolves in hot water.

It will be recognised that the behaviour of the substance  $C_{10}H_{14}O_5N_2$  is remarkable, because, although its production by the action of potassium ferricyanide on an oximino-compound would suggest its classification as a secondary nitro-derivative, nevertheless, the acidity which characterises it is more pronounced than that of many carboxylic acids; if it belonged to the latter class, the indifference towards hydrogen chloride of a solution in methyl alcohol would be explained if the group were attached to tertiary carbon. The compound, however, although optically active to a slight extent only, exhibits definite mutarotation, and we think that this fact, in conjunction with the experiments still to be described, is evidence in support of the view that it is a secondary nitro-derivative.

A solution containing 1.1925 grams in 25 c.c. of chloroform at  $20^{\circ}$  was prepared in a darkened room, and transferred to the 2-dcm. tube

without more than a minute's interval after dissolution; the reading observed was  $21'$ , which fell to  $10'$  while confirmatory observations were being made. In half an hour, the solution gave  $\alpha_D -39'$ , remaining constant at  $\alpha_D -1^\circ 8'$ , which was reached on the eleventh day. Thus, the initial and final specific rotatory powers are  $[\alpha]_D +3.6^\circ$  and  $[\alpha]_D -11.9^\circ$  respectively.

*Action of Potassium Hypobromite.*—Ten grams were dissolved in aqueous potassium hydroxide and treated with potassium hypobromite prepared by adding 20 grams of bromine to an ice-cold, concentrated solution of caustic potash. A snow-white precipitate was formed immediately, and this was filtered, washed, and crystallised from hot alcohol, which deposited 13 grams; on recrystallisation, it was obtained in colourless needles melting at  $157^\circ$ .

0.3314 gave  $0.4543 \text{ CO}_2$  and  $0.1106 \text{ H}_2\text{O}$ .  $\text{C} = 37.39$ ;  $\text{H} = 3.73$ .

0.2336 „  $0.1367 \text{ AgBr}$ .  $\text{Br} = 24.90$ .

$\text{C}_{10}\text{H}_{13}\text{O}_5\text{N}_2\text{Br}$  requires  $\text{C} = 37.38$ ;  $\text{H} = 4.05$ ;  $\text{Br} = 24.92$  per cent.

A solution containing 1.2415 grams in 25 c.c. of chloroform at  $20^\circ$  gave  $\alpha_D -6^\circ 45'$  in a 2-dcm. tube, whence  $[\alpha]_D -68.0^\circ$ .

The substance dissolves sparingly in boiling light petroleum, from which it separates in minute needles, and is moderately soluble in benzene, alcohol, ethyl acetate, or glacial acetic acid, crystallising from the first named in well-formed, six-sided prisms; acetone and chloroform dissolve it freely. The Liebermann reaction is very intense in all its stages. When the bromo-derivative is heated with alcoholic potash, the compound  $\text{C}_{10}\text{H}_{14}\text{O}_5\text{N}_2$  is regenerated.

*Action of Hydroxylamine.*—Ten grams of the substance were dissolved in 250 c.c. of absolute alcohol, and treated first with 20 grams of hydroxylamine hydrochloride and then with 18.7 grams of potassium hydroxide, both dissolved in water; after 2 hours on the water-bath, the liquid was evaporated and filtered from the solid (1.2 grams) which separated on cooling. The filtrate was faintly alkaline and yielded a colourless precipitate (6.1 grams) on acidification. Both products were then crystallised from hot water, which deposited the former in lustrous, orange leaflets melting at  $184^\circ$ .

0.1709 gave 19.4 c.c. nitrogen at  $20^\circ$  and 749 mm.  $\text{N} = 12.80$ .

$\text{C}_{10}\text{H}_{14}\text{O}_4\text{N}_2$  requires  $\text{N} = 12.39$  per cent.

The substance is moderately soluble in alcohol, from which it crystallises in thin, striated prisms. It dissolves in 2 per cent. sodium hydroxide, but gives no coloration with ferrous sulphate, and does not reduce Fehling's solution, although ammoniacal silver nitrate is reduced immediately on boiling. The alcoholic solution develops an intense purple coloration with ethereal ferric chloride, and, when

treated with copper acetate in alcohol, destroys the colour of the first few drops and quickly yields a sage-green precipitate. It does not give Liebermann's reaction.

The second product dissolves more readily in sodium carbonate than the foregoing substance, and crystallises from boiling water in colourless, transparent pyramids melting at  $161^{\circ}$ , the solution being acid to litmus.

0.3924 gave 26.4 c.c. nitrogen at  $19^{\circ}$  and 748 mm.  $N = 7.61$ .

$C_{10}H_{15}O_3N$  requires  $N = 7.10$  per cent.

This compound gives no coloration with ethereal ferric chloride, and reduces ammoniacal silver nitrate very slightly on continued boiling. It does not give Liebermann's reaction, and gives no characteristic precipitate in 2 per cent. sodium hydroxide with ferrous sulphate or with potassium hypobromite. It is practically insoluble in light petroleum, dissolves very sparingly in chloroform and carbon bisulphide, and is only moderately soluble in hot alcohol or acetone. It neither decolorises dissolved bromine nor yields hydrogen bromide when warmed with the halogen, but the sodium carbonate solution reduces potassium permanganate freely.

*Reduction with Sodium Amalgam.*—By this treatment, the compound  $C_{10}H_{14}O_5N_2$  is converted into a deep red substance, and hydroxylamine is eliminated.

Ten grams were dissolved in 50 c.c. of 10 per cent. sodium hydroxide and shaken with 360 grams of 2 per cent. sodium amalgam, which was added in quantities of 40 grams at intervals of half an hour, the liquid being kept cool and diluted occasionally with a few c.c. of water. With the first addition of amalgam, a turbidity appeared, followed by a pink coloration, which rapidly deepened to an intense dark red tint; meanwhile, an ammoniacal odour became noticeable. When all the reducing agent had been used, a few c.c. of sodium carbonate were added, so that the product being soluble in both acids and alkalis, the next step, acidification, can be interrupted when effervescence begins. A vermilion precipitate was thus obtained, and the filtrate reduced cold Fehling's solution immediately.

The substance could not be recrystallised, but a specimen reprecipitated from a filtered solution in 10 per cent. potassium hydroxide was analysed.

0.1991 gave 15.2 c.c. nitrogen at  $17^{\circ}$  and 772 mm.  $N = 9.00$ .

$C_{10}H_{15}ON$  requires  $N = 8.48$  per cent.

$C_{20}H_{30}ON_2$  „  $N = 8.92$  „

It is insoluble in light petroleum, but dissolves very freely in cold alcohol and in boiling water, forming red solutions which have no

action on ammoniacal silver nitrate and Fehling's solution respectively. The solution in dilute sulphuric acid has the colour of potassium permanganate, and the wine-red liquid produced by dissolving the substance in 2 per cent. sodium hydroxide yields a dark brown precipitate with ferrous sulphate. An alcoholic solution gives no distinctive coloration with ethereal ferric chloride, but develops a magnificent purple with potassium hydroxide.

*Action of Potassium Hypobromite on the Green Oil.*

Ten grams of the nitrosate were suspended in 75 c.c. of absolute alcohol and heated on the water-bath during 2 hours with 7 grams of caustic potash dissolved in the minimum quantity of water; the residue obtained on evaporation having been dissolved in ice-cold water, a freshly prepared solution of potassium hypobromite containing 30 grams of bromine was added. A heavy, yellow oil was precipitated, hardening immediately on treatment with cold water, and weighing 15 grams.

This compound has been obtained also by treating with excess of potassium hypobromite the brown alkaline liquid formed on shaking with aqueous potash the green chloroform filtrate from the nitrosate; 16 grams were thus produced from 25 grams of nitrocamphene.

The substance prepared by these methods dissolves in boiling light petroleum, and crystallises in stellate aggregates of lustrous, pale brown prisms melting at 78°.

0.3201 gave 0.3040 CO<sub>2</sub> and 0.0885 H<sub>2</sub>O. C = 25.90; H = 3.09.

0.4382 „ 22.6 c.c. nitrogen at 20° and 763 mm. N = 5.93.

0.2542 „ 0.2971 AgBr. Br = 49.73.

C<sub>10</sub>H<sub>11</sub>O<sub>5</sub>N<sub>2</sub>Br<sub>3</sub> requires C = 25.05; H = 2.30; N = 5.84; Br = 50.10 per cent.

It is readily soluble in cold chloroform and ethyl acetate, and less freely in alcohol and acetic acid. A solution containing 1.2882 grams in 25 c.c. of chloroform at 20° gives  $\alpha_D^{26}$  in a 2-dcm. tube, whence  $[\alpha]_D + 4.2^\circ$ . Although it undergoes reduction in alcoholic solution with zinc dust, aluminium amalgam, and with potassium hydroxide, in no case has a crystalline product been obtained. The tribromo-derivative gives Liebermann's reaction with great intensity in all its stages.

*Methylaminocamphene, C<sub>10</sub>H<sub>15</sub>·NH·CH<sub>3</sub>.*

At one time it seemed possible that the object we had in view might be attained by the use of derivatives of aminocamphene, and experiments were made with benzoylaminocamphene and methyl-

aminocamphene, but without success. The latter substance was obtained by the process devised for the preparation of methylbornylamine (Trans., 1899, 75, 936); this consists in converting the benzylidene derivative of the primary base into the methiodide, and heating this with moist ethyl acetate, which hydrolyses it to benzaldehyde and the hydriodide of the methylated base.

Six grams of benzylideneaminocamphene (Trans., 1901, 79, 650) were heated in a sealed tube with 22 grams of methyl iodide at  $100^{\circ}$  during 2 hours, the product being treated with ether and filtered. The yellow crystals weighed 7 grams and had a faint odour of benzaldehyde.

0.1309 gave 0.0828 AgI.  $I = 34.19$ .

0.2188 „ 0.1418 AgI.  $I = 34.21$ .

$C_{10}H_{15} \cdot N \cdot CH \cdot C_6H_5, CH_3I$  requires  $I = 33.34$  per cent.

Twenty-eight grams of this material were heated with 200 c.c. of undried ethyl acetate during 1 hour; 21 grams of methylaminocamphene hydriodide were obtained and recrystallised from hot water.

0.2040 gave 0.1632 AgI.  $I = 43.23$ .

$C_{11}H_{20}NI$  requires  $I = 43.34$  per cent.

On decomposing the salt with caustic alkali, methylaminocamphene was obtained as a colourless oil which boils at  $202-203^{\circ}$  under 756 mm. pressure, and has sp. gr. 0.9171 at  $22^{\circ}$ . A solution containing 0.5447 gram in 25 c.c. of absolute alcohol gave  $\alpha_D 1^{\circ}17'$  in a 2-dcm. tube, whence  $[\alpha]_D + 28.7^{\circ}$ .

The *platinichloride* melts and decomposes at  $214^{\circ}$ .

0.1322 gave 0.0349 Pt.  $Pt = 26.39$ .

0.2893 „ 0.0763 Pt.  $Pt = 26.37$ .

$(C_{11}H_{19}N)_2, H_2PtCl_6$  requires  $Pt = 26.27$  per cent.

The salt dissolves readily in alcohol, from which it crystallises in minute needles.

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XXXVII.—*The So-called "Hydrocellulose."*

By ARTHUR LANDAUER STERN, D.Sc.

It is well known that all kinds of cellulose, when exposed to the action of certain reagents, lose their tenacity and become friable. This fact has hitherto been explained as being the result of the hydration of the cellulose, leading to the formation of hydrocellulose. All the evidence concerning this change appears to be contained in the work of A. Girard (*Compt. rend.*, 1875, **81**, 1105—1108; 1879, **88**, 1322—1324; and *Ann. Chim. Phys.*, 1881, [v], **24**, 337—384), who prepared hydrocellulose by several different methods, and having determined its empirical composition found this to agree fairly well with the formula  $C_{12}H_{22}O_{11}$ . The results of certain experiments carried out by the author in the course of another investigation threw doubt on the accuracy of Girard's observations, and consequently some of his experiments were repeated.

Girard prepared hydrocellulose by treating cellulose with cold sulphuric acid (sp. gr. 1.45), by the action of cold moist hydrogen chloride on air-dried cellulose, and by heating cellulose with dilute acids. The attempts made to prepare hydrocellulose by the first two of these methods proved unsuccessful, but the action of boiling 5 per cent. sulphuric acid on flax or cotton cellulose soon destroyed the tenacity of the fibres and converted the substance into a friable mass.

As the change of  $2C_6H_{10}O_5$  into  $C_{12}H_{22}O_{11}$  is accompanied by an increase in weight of 5.6 per cent., it should be possible to detect this by quantitative experiments. Girard, however, states that under the most favourable conditions the weight of hydrocellulose obtained is less than the weight of the original cellulose, and he explains this discrepancy by assuming that *d*-glucose is simultaneously produced, but adduces no evidence in support of this assumption beyond the fact that, after the reaction, the acid solution reduces Fehling's solution.

Experiments made to determine the relation between the weight of the cellulose taken and (*A*) the weight of the hydrocellulose and (*B*) the weight and nature of the other products of the reaction, gave the following results.

A. (1) Flax cellulose, boiled for  $2\frac{1}{4}$  hours in 5 per cent. sulphuric acid, lost 2.1 per cent., and was reduced to a powder.

(2) Cotton cellulose, boiled for 1 hour with 5 per cent. sulphuric acid, similarly lost 3.9 per cent.

(3) Cotton cellulose, immersed in sulphuric acid (sp. gr. 1.45) for 16 hours at 26°, lost 3.3 per cent.; the fibres were rendered brittle, but were not converted into a powder.

The following experiments show that this loss in weight is not a peculiar concomitant of the conversion of cellulose into hydrocellulose, but also occurs when hydrocellulose itself is submitted to the further action of the acid. The flax cellulose, which had been converted into hydrocellulose in the manner indicated by boiling with 5 per cent. sulphuric acid for 2½ hours, was again submitted to the same process, when a further loss of 1.9 per cent. was observed, and the treatment being again repeated on the hydrocellulose remaining, there was an additional loss of 2.0 per cent.

*B.* About 380 grams of purified cotton cellulose, covered with 5 per cent. sulphuric acid, were digested at 100° for 4 hours; the soluble matter was then filtered off and the "hydrocellulose" produced thoroughly washed with water. The sulphuric acid was removed from the solution by neutralisation with baryta, the precipitated barium sulphate filtered off, and the filtrate evaporated to a syrup *in vacuo*. This residue was treated with methyl alcohol, in which the greater portion dissolved. The total soluble products of the hydrolysis weighed 6.4 grams, or 1.8 per cent. of the cellulose employed.

The syrup, which was uncrystallisable, had an optical activity of +37° and a cupric reducing power  $K = 90$  (*d*-glucose having  $K = 100$ ). A portion of the syrup, when treated with phenylhydrazine acetate in the usual way, yielded a golden-yellow osazone closely resembling glucosazone, which crystallised in needles and melted at 208°. Another portion, to which a small quantity of yeast had been added, lost 60 per cent. of its optical activity in a few days; the optical activity of the matter fermented was  $[\alpha]_D = 48^\circ$ , and its  $K = 107$ . All these facts indicate that one of the soluble products of the hydrolysis is *d*-glucose; the amount obtained is, however, insufficient to explain Girard's theory that the deficiency in the yield of hydrocellulose which is always found may be explained by the conversion of this deficiency into *d*-glucose.

The production of *d*-glucose in the conversion of ordinary cellulose into hydrocellulose is not, however, a peculiar characteristic of this change, as it is also formed when hydrocellulose is further acted on by hot dilute sulphuric acid. The hydrocellulose obtained in the last transformation was treated for a further period of 4 hours with 5 per cent. sulphuric acid at 100°. The soluble products of the transformation, when separated in the same way, amounted to 5.3 grams, or 1.5 per cent. of the weight of hydrocellulose taken. A methyl-alcoholic solution of the syrupy product deposited crystals which had the following properties :  $c = 7.517$  ;  $D = 3.972$  ;  $[\alpha]_D = 36.9^\circ$  ;

and, after recrystallisation, gave the following data:  $c = 2.582$ ;  $D = 3.916$ ;  $[\alpha]_D = 45.9^\circ$ ;  $K = 95.2$ .\*

A solution of the recrystallised product, when fermented with a small quantity of yeast, lost 58 per cent. of its optical activity in a few days, and another portion yielded a yellow, crystalline osazone resembling glucosazone and melting at  $208^\circ$ .

The hydrocellulose residue of this reaction, when again treated in the same way, yielded 4.0 grams of soluble products, the methyl-alcoholic solution of which deposited crystals having the following properties:  $c = 4.778$ ;  $D = 3.926$ ;  $[\alpha]_D = 47.3^\circ$ ;  $K = 97.5$ . A portion put to ferment with yeast lost 61 per cent. of its optical activity in a few days, and another portion yielded a yellow, crystalline osazone melting at  $210^\circ$ .

The hydrocellulose residue now remaining was again treated as before and 2.5 grams of soluble products were obtained, the methyl-alcoholic syrup of which gave crystals having the following properties;  $c = 4.195$ ;  $D = 3.893$ ;  $[\alpha]_D = 45.6^\circ$ ;  $K = 97.8$ . A portion of this substance, when fermented with yeast for 10 days, a longer time than the previous fermentations, lost 97.8 per cent. of its optical activity, and another portion gave a yellow, crystalline osazone melting at  $204^\circ$ .

*Analysis of Hydrocellulose.*—Girard's results, which vary between 41.8 and 42.1 per cent. of carbon and 6.3—6.7 per cent. of hydrogen, although not very satisfactory, yet agree moderately well with the empirical formula  $C_{12}H_{22}O_{11}$ , which requires 42.1 per cent. of carbon and 6.4 per cent. of hydrogen.

The celluloses employed in the present experiments were burnt before and after having been exposed to the action of acids as described above and yielded the following results:

	Flax cellulose.	Flax cellulose after the action of sulphuric acid. Sp. gr. 1.45, not friable.	Flax cellulose reduced to powder by the action of 5 per cent. sulphuric acid for two hours at $100^\circ$ .	Flax cellulose after being treated with 5 per cent. sulphuric acid for 7 hours at $100^\circ$ .	Cotton cellulose.	Cotton cellulose reduced to powder by the action of 5 per cent. sulphuric acid at $100^\circ$ .	Cotton cellulose after the action of sulphuric acid. Sp. gr. 1.45 at $26^\circ$ , very brittle.	Theory for $C_6H_{10}O_5$ .
Carbon .....	44.28	44.39	44.44	44.27	44.45	44.38	44.31	44.42
Hydrogen ...	6.28	6.28	6.26	6.24	6.32	6.27	6.29	6.22

\*  $c$  = Concentration in grams per 100 c.c.  $D$  = Divisor; a factor obtained by dividing the specific gravity minus 1, by  $c$  and multiplying the result by 1000.  $K$  = Cupric reducing power compared with that of *d*-glucose as 100.

These figures agree very closely with the formula  $C_6H_{10}O_5$ .

It appeared at first difficult to understand how Girard came to obtain his analytical figures, but this investigator's account of his experiments will render this quite clear. He states that hydrocellulose is easily oxidised on exposure to warm air; at  $80^\circ$ , it becomes coloured, and at  $100^\circ$  this change takes place very rapidly. In several of the author's experiments, it was found that, after the action of the acid, the cellulose, when washed in the usual way, was blackened on drying at  $100^\circ$ , but in every case in which this took place, sulphuric acid was detected in the filtrate obtained by extracting the blackened mass with hot water. On the other hand, all the preparations of which the analyses are given above were dried in a current of dry air at  $100^\circ$ ; in no case was the slightest colour produced, and the preparations did not contain sulphuric acid. As Girard's preparations became coloured when exposed to a temperature of  $100^\circ$ , it is evident that they must have contained free acid, and as, on account of this, he only dried them at  $35-40^\circ$ , it is extremely probable that they also contained water, and hence the low numbers obtained for the carbon and the high values for the hydrogen are explained. One of the author's specimens prepared by the action of sulphuric acid (sp. gr. 1.45) at  $25^\circ$  gave only 44.05 as the percentage of carbon, but in washing this specimen free from acid, a little ammonia had been added to one of the wash waters, and although it was thought that the cellulose had been properly washed, yet when another portion of the specimen was extracted with hot water, sulphuric acid was found in the filtrate, showing that a small amount of sulphate had been contained in the specimen burnt, thus accounting for the low percentage of carbon.

It is evident from a consideration of these results that when cellulose is exposed to the action of hot dilute acids there is no formation of hydrocellulose; the cellulose is partly hydrolysed with the production of soluble products, one of which is in all probability *d*-glucose. The cellulose residue, after exposure to the action of hot dilute acid for some hours, does not differ in elementary composition from the original cellulose, but has been converted into a fine powder. A microscopic examination of the disintegrated cellulose at different stages of the reaction, shows that the disintegration is due to the fact that certain portions of the fibre are more easily attacked than others, and when these portions of the fibres are converted into soluble products the whole fibre falls to pieces. Although this change is most marked in the first stage of the reaction, yet each successive digestion results in the production of a finer product, until that obtained in the above-described experiments, after treatment for 16 hours, was so fine as to be most difficult to filter.

The slowness of the action and the consequent long period of time

during which it was necessary to allow the hydrolysis to proceed in order to obtain a sufficient amount of soluble products, rendered it impossible to decide whether *d*-glucose was the only product of the hydrolysis or whether, as seems probable from Fenton's experiments, there are other soluble products (Trans., 1 98, 73, 554; 1899, 75, 423; 1901, 79, 361 and 807; and Proc., 1901, 17, 166). Lævulose, for example, would be destroyed in the foregoing experiments, owing to the protracted action of the hot acids.

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### XXXVIII.—*Intramolecular Rearrangement in Derivatives of the Aromatic Aminoketones.*

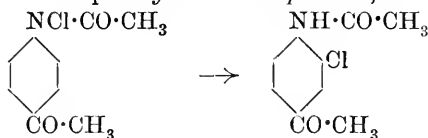
By FREDERICK DANIEL CHATTAWAY.

THE acylchloroamino-derivatives of the aromatic ketones readily undergo the intramolecular rearrangement characteristic of aromatic chloroamides, in which the halogen radicle leaves the nitrogen and changes place with a hydrogen atom occupying an ortho- or para-position in the ring. The presence of the ketonic group does not, apparently, influence the rearrangement. As, however, the final transformation whereby both vacant positions are filled only takes place at a somewhat high temperature, the ketonic group becomes involved under the influence of the catalyst employed, uncrystallisable tarry substances are produced, and the yield of the disubstituted aminoketone is small.

By these intramolecular changes, a number of substituted amino-ketones have been prepared, which are not easily obtained by direct substitution, this reaction as a rule only yielding a tarry product from which no pure substance can be isolated.

The mode in which these substituted ketones are produced fixes their constitution, as in such transformations the halogen is known always to take up the para- in preference to the ortho-position, whilst the meta-position with respect to the amino-group is never assumed.

*Transformation of Acetyl-p-chloroaminoacetophenone into 3-Chloro-p-acetylaminoacetophenone,*

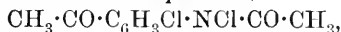


This transformation slowly takes place when a solution of the chloroamide in chloroform containing about 5 per cent. of acetic acid is allowed to remain at the ordinary temperature, light being excluded; the change is complete in about 14 days. On evaporating off the chloroform, a red solid is left from which 3-chloro-p-acetylaminoacetophenone can be obtained by repeated crystallisation from alcohol. This substance crystallises in slender, colourless prisms (m. p. 163°).

0.3635 yielded 0.2520 AgCl. Cl = 17.17.

$\text{C}_{10}\text{H}_{10}\text{O}_2\text{NCl}$  requires Cl = 16.75 per cent.

*3-Chloro-p-acetylchloroaminoacetophenone,*



was prepared by adding a solution of 3-chloro-4-acetylaminoacetophenone dissolved in alcohol to an ice-cold solution of potassium hypochlorite containing an excess of potassium hydrogen carbonate; it was extracted by chloroform, and, to complete the action, the solution was repeatedly shaken with fresh hypochlorous acid. The compound crystallises from petroleum (b. p. 60–80°) in clusters of colourless, transparent plates (m. p. 56°).

0.1746 liberated I = 13.8 c.c. N/10 I. Cl (as NCl) = 14.01.

$\text{C}_{10}\text{H}_9\text{O}_2\text{NCl}_2$  requires Cl (as NCl) = 14.41 per cent.

When dissolved in glacial acetic acid and heated, it undergoes transformation, but the quantity of the crystalline dichloro-transformation product which could be isolated from the tarry product of the action was so small that it was not further studied.

*3-Chloro-p-aminoacetophenone,*  $\text{CH}_3 \cdot \text{CO} \cdot \text{C}_6\text{H}_3\text{Cl} \cdot \text{NH}_2$ , was prepared by hydrolysing the acetyl derivative by heating it for four hours with a mixture of alcohol and concentrated hydrochloric acid and decomposing the hydrochloride of the base with caustic potash. It crystallises from a mixture of chloroform and petroleum in short, four-sided, colourless prisms (m. p. 92°).

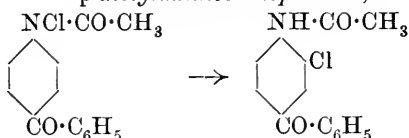
0.1959 yielded 0.1668 AgCl. Cl = 21.05.

$\text{C}_8\text{H}_8\text{ONCl}$  requires Cl = 20.91 per cent.

3-Chloro-p-benzoylaminoacetophenone,  $\text{CH}_3 \cdot \text{CO} \cdot \text{C}_6\text{H}_4\text{Cl} \cdot \text{NH} \cdot \text{CO} \cdot \text{C}_6\text{H}_5$ , crystallises from alcohol in slender, colourless needles (m. p.  $132^\circ$ ).

3-Chloro-p-propionylaminoacetophenone,  
 $\text{CH}_3 \cdot \text{CO} \cdot \text{C}_6\text{H}_4\text{Cl} \cdot \text{NH} \cdot \text{CO} \cdot \text{C}_2\text{H}_5$ ,  
 crystallises from a mixture of chloroform and petroleum in groups of slender, colourless needles (m. p.  $115^\circ$ ).

*Transformation of Acetyl-p-chloroaminobenzophenone into 3-Chloro-p-acetylaminobenzophenone,*

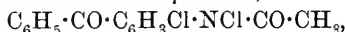


This transformation takes place slowly under similar conditions to those which bring about the transformation of the acetophenone derivative. When the chloroamide dissolved in chloroform containing 5 per cent. glacial acetic acid was allowed to remain at the ordinary temperature and screened from light, it became completely transformed in about 14 days. On evaporating off the chloroform, a viscid, oily substance was left, which, however, solidified to a nearly colourless mass on warming for a short time with a solution of potassium hydrogen carbonate. When repeatedly crystallised from alcohol, the pure 3-chloro-4-acetylaminobenzophenone,  $\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{C}_6\text{H}_3\text{Cl} \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}_3$ , was obtained in colourless, rhombic plates (m. p.  $99.5^\circ$ ).

0.2440 gave 0.1265 AgCl. Cl = 12.82.

$\text{C}_{15}\text{H}_{12}\text{O}_2\text{NCl}$  requires Cl = 12.96 per cent.

3-Chloro-p-acetylchloroaminobenzophenone,



crystallises from a mixture of chloroform and petroleum (b. p.  $60-80^\circ$ ) in transparent, colourless plates (m. p.  $102^\circ$ ).

0.3760 liberated I = 24.5 c.c.  $N/10$  I. Cl (as NCl) = 11.55.

$\text{C}_{15}\text{H}_{11}\text{O}_2\text{NCl}_2$  requires Cl (as NCl) = 11.51 per cent.

3-Chloro-p-aminobenzophenone,  $\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{C}_6\text{H}_3\text{Cl} \cdot \text{NH}_2$ , was obtained by heating the acetyl derivative for three hours on a water-bath with alcoholic hydrochloric acid and decomposing the hydrochloride of the base with caustic potash; it crystallises from a mixture of chloroform and petroleum in small, slender, colourless prisms (m. p.  $140^\circ$ ).

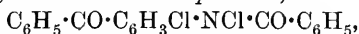
0.1942 gave 0.1209 AgCl. Cl = 15.39.

$\text{C}_{13}\text{H}_{10}\text{ONCl}$  requires Cl = 15.31 per cent.

3-Chloro-p-benzoylaminoacetophenone,  $\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{C}_6\text{H}_3\text{Cl} \cdot \text{NH} \cdot \text{CO} \cdot \text{C}_6\text{H}_5$ ,

is sparingly soluble in alcohol, from which it crystallises in colourless, flattened prisms (m. p. 126°).

*3-Chloro-p-benzoylchloroaminobenzophenone,*

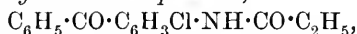


crystallises from light petroleum in short, colourless, flattened prisms with domed ends (m. p. 123°).

0.1404 liberated I = 7.5 c.c. *N*/10 I. Cl (as NCl) = 9.46.

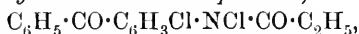
$\text{C}_{20}\text{H}_{13}\text{O}_2\text{NCl}_2$  requires Cl (as NCl) = 9.58 per cent.

*3-Chloro-p-propionylaminobenzophenone,*



crystallises from alcohol or a mixture of chloroform and petroleum in slender, colourless needles (m. p. 107.5°).

*3-Chloro-p-propionylchloroaminobenzophenone,*



crystallises from a mixture of chloroform and petroleum in colourless plates (m. p. 114°).

0.2790 liberated I = 17.4 c.c. *N*/10 I. Cl (as NCl) = 11.05.

$\text{C}_{16}\text{H}_{13}\text{O}_2\text{NCl}_2$  requires Cl (as NCl) = 11.01 per cent.

*Transformation of Acetyl-o-chloroaminobenzophenone into 5-Chloro-o-acetylaminobenzophenone,*



This compound does not become transformed nearly so readily as the corresponding para-derivative, and remains apparently unchanged in chloroform solution containing 5 per cent. of acetic acid for a period sufficient for the complete transformation of the latter.

This transformation can, however, be effected, accompanied by some decomposition and the formation of tarry products, by dissolving the chloroamide in glacial acetic acid containing about 0.5 per cent. of hydrogen chloride and heating the solution in a sealed tube in a water-bath for a few hours. On pouring the product into water and washing with a dilute solution of potassium hydrogen carbonate in order to remove the acid, a pale brown, tarry mass is obtained. On dissolving this in a little alcohol, the transformation product slowly separates in colourless needles.

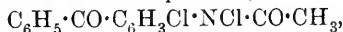
The behaviour of all similar derivatives leaves no doubt that the chlorine passes almost exclusively into the para-position with regard to the acetylamino-group.

5-Chloro-o-acetylaminobenzophenone,  $C_6H_5 \cdot CO \cdot C_6H_3Cl \cdot NH \cdot CO \cdot CH_3$ , crystallises from alcohol in slender, colourless prisms (m. p. 117°).

0.2103 yielded 0.1104 AgCl.  $Cl = 12.98$ .

$C_{15}H_{12}O_2NCl$  requires  $Cl = 12.96$  per cent.

5-Chloro-o-acetylchloroaminobenzophenone,



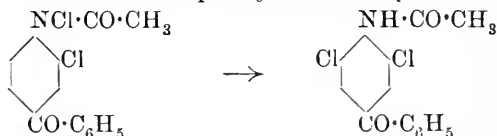
crystallises from a mixture of chloroform and petroleum in clusters of colourless plates (m. p. 107°).

0.2599 liberated  $I = 16.8$  c.c.  $N/10$  I.  $Cl$  (as  $NCl$ ) = 11.46.

$C_{15}H_{11}O_2NCl_2$  requires  $Cl$  (as  $NCl$ ) = 11.51 per cent.

5-Chloro-o-aminobenzophenone,  $C_6H_5 \cdot CO \cdot C_6H_3Cl \cdot NH_2$ .—The acetyl derivative of this base is hydrolysed only with difficulty, and requires prolonged boiling with excess of alcoholic hydrochloric acid. 5-Chloro-2-aminobenzophenone is readily soluble in chloroform or alcohol, sparingly so in petroleum; it crystallises from a mixture of chloroform and light petroleum in slender, yellow needles (m. p. 100°).

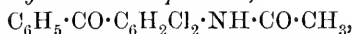
*Transformation of 3-Chloro-p-acetylchloroaminobenzophenone into 3:5-Dichloro-p-acetylaminobenzophenone,*



The transformation of the acylchloroaminobenzophenones is exactly analogous to that of the acylchloroamino-derivatives of the similarly constituted chloroanilines. The transformation of acetyl-p-chloroaminobenzophenone is effected more readily than that of acetyl-o-chloroaminobenzophenone, and the transformation of the latter more readily than that of 3-chloro-p-acetylchloroaminobenzophenone. Even when dissolved in glacial acetic acid containing a little hydrogen chloride and heated at 100° for several hours, this compound undergoes no appreciable amount of transformation.

Intramolecular rearrangement, however, occurs when the solution is heated for some hours at 130–140°; after eight hours at this temperature, the chloroamide was found to have completely disappeared. On diluting the product and adding a slight excess of potassium hydrogen carbonate to neutralise the acid, a pale yellow, viscid mass was obtained which was readily soluble in warm alcohol, the solution slowly depositing needle-shaped crystals of the transformation product. The yield, however, is small, a considerable quantity of a tarry substance being formed,

3 : 5-Dichloro-p-acetylaminobenzophenone,



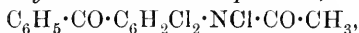
crystallises from alcohol in colourless, needle-shaped crystals (m. p. 185°).

0.1626 gave 0.1509 AgCl.  $\text{Cl} = 22.94$ .

$\text{C}_{15}\text{H}_{11}\text{O}_2\text{NCl}_2$  requires  $\text{Cl} = 23.02$  per cent.

The constitution of the compound follows from its mode of preparation, as the chlorine atoms can only enter the ortho-positions with respect to the acetyl-amino-group.

3 : 5-Dichloro-p-acetylchloroaminobenzophenone,



crystallises from a mixture of chloroform and petroleum in groups of transparent, colourless plates (m. p. 118°).

0.1019 liberated  $\text{I} = 5.9$  c.c.  $\text{N}/10$  I.  $\text{Cl}$  (as  $\text{NCl}$ ) = 10.26.

$\text{C}_{15}\text{H}_{10}\text{O}_2\text{NCl}_3$  requires  $\text{Cl}$  (as  $\text{NCl}$ ) = 10.35 per cent.

3 : 5-Dichloro-p-aminobenzophenone,  $\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{C}_6\text{H}_2\text{Cl}_2 \cdot \text{NH}_2$ , prepared by hydrolysing the acetyl compound by boiling with alcoholic hydrochloric acid, crystallises from alcohol in short, colourless prisms (m. p. 137°).

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### XXXIX.—The Separation of $\beta$ -Crotonic Acid from $\alpha$ -Crotonic Acid.

By ROBERT SELBY MORRELL and ALBERT ERNEST BELLARS.

THE separation of  $\beta$ -crotonic acid from  $\alpha$ -crotonic acid is effected, according to Michael and Schulthess (*J. pr. Chem.*, 1892, [ii], 46, 245), by means of the different solubilities of the sodium salts in alcohol. One part of sodium  $\alpha$ -crotonate dissolves in 340 parts of alcohol (98—99 per cent.) at 15°, whilst at the same temperature, one part of sodium  $\beta$ -crotonate requires 12.7 parts of alcohol of the same strength; the more soluble  $\beta$ -crotonate is then decomposed by hydrochloric acid, and the free acid purified by distillation *in vacuo*.  $\beta$ -Crotonic acid, obtained by Michael's method or by the method described by Fittig and Kochs (*Annalen*, 1892, 268, 15), is stated by J. Wislicenus (*Chem. Centr.*, 1897, ii, 259) to contain  $\alpha$ -crotonic acid, in spite of Michael's acid giving no precipitate in alcoholic precipitate on neutralisation

with alcoholic sodium hydroxide. The pure acid has been obtained (J. Wislicenus, *loc. cit.*) by transforming liquid  $\beta$ -crotonic acid, dissolved in alcohol, into its sodium salt, and by removing the sodium  $\alpha$ -crotonate by concentrating the solution and precipitating the last traces of the salt by the addition of an equal volume of ether; the sodium  $\beta$ -crotonate left in solution is decomposed by hydrochloric acid, and the acid, which is purified by recrystallisation from pentane, crystallises in needles or prisms melting at  $15.45-15.5^{\circ}$ ; the yield must be small, and the method of preparation seems tedious.

In a paper by one of us (Morrell and Hanson, *Trans.*, 1904, 85, 197), the optically active constituents of  $\alpha\beta$ -dihydroxybutyric acid, prepared from  $\alpha$ -crotonic acid, were described, and it was stated that the optically active constituents of a second  $\alpha\beta$ -dihydroxybutyric acid were under investigation.

The oxidation of "*isocrotonic*" acid, supplied by Kahlbaum, gave an acid the brucine and quinine salts of which were virtually identical with those of symmetrical  $\alpha\beta$ -dihydroxybutyric acid, so that it was necessary to devise a method of separation of the two isomeric acids, and to prepare salts of  $\beta$ -crotonic acid, which are less soluble than the corresponding  $\alpha$ -crotonates. The brucine salts of the two acids were found to have different solubilities, and the  $\beta$ -acid yielded the less soluble salt, but unfortunately these salts are very soluble in all ordinary solvents. The quinine salts, however, are sparingly soluble in water, and the salt of the  $\beta$ -acid is much less soluble than that of the  $\alpha$ -acid; it is therefore quite easy to separate the two salts by crystallisation from water, and the quinine  $\beta$ -crotonate can be recrystallised from that solvent without undergoing any change in melting point. From the quinine salt, the barium  $\beta$ -crotonate has been prepared, and this has given the pure acid by treatment with dilute sulphuric acid in the presence of pure ether. The melting point agrees with that given by Wislicenus, namely,  $15^{\circ}$ . Determinations of the density, molecular weight, and molecular refraction have been made. The molecular weight in glacial acetic acid solution corresponds with the formula  $C_4H_6O_2$ , and there seems no justification for the double formula proposed by Wislicenus (*Chem. Centr.*, 1897, ii, 259).

Michael and Schulthess (*loc. cit.*) state that the purity of  $\beta$ -crotonic acid can be shown by neutralising its alcoholic solution with 10 per cent. caustic soda solution; sodium  $\beta$ -crotonate is very soluble in alcohol, and, under the experimental conditions, no precipitate ought to be formed on neutralisation. We have tested the  $\beta$ -crotonic acid prepared from the quinine salt, following Michael's directions, and have found that no insoluble sodium crotonate was formed; moreover, the determination of the solubility of sodium  $\beta$ -crotonate gave values agreeing with those obtained by Michael.

## EXPERIMENTAL.

*Brucine  $\alpha$ -Crotonate.*—This salt, which was prepared by neutralising a boiling aqueous solution of  $\alpha$ -crotonic acid with brucine, is exceedingly soluble in water, alcohol, or benzene; 5 grams dissolve in 7 c.c. of hot benzene, and the salt slowly crystallises out in hexagonal prisms, which soften at  $90^\circ$  and melt at  $125^\circ$ .

*Quinine  $\alpha$ -Crotonate.*—This salt crystallises from a hot aqueous solution in aggregates of slender needles, which melt at  $136^\circ$  without decomposition; a solubility determination at  $17^\circ$  showed that 0.3203 gram was dissolved in 13.7 grams of solution, hence the solubility of the salt in water at  $17^\circ$  is 2.4.

*"isocrotonic" Acid.*—The acid was obtained from Kahlbaum, who stated that it was prepared by heating  $\beta$ -hydroxybutyric acid, and freed from  $\alpha$ -crotonic acid, as far as possible, by distillation *in vacuo* and by freezing out the last traces of the  $\alpha$ -isomeride at  $-20^\circ$ . Several analyses of the acid were made, but the percentages of carbon were invariably found to be too low (compare Michael and Schulthess, *loc. cit.*).

0.1845 gave 0.3732  $\text{CO}_2$  and 0.1145  $\text{H}_2\text{O}$ . C = 55.16; H = 6.89.

0.1950 ,, 0.3920  $\text{CO}_2$  ,, 0.1243  $\text{H}_2\text{O}$ . C = 54.82; H = 7.08.

$\text{C}_4\text{H}_6\text{O}_2$  requires C = 55.8; H = 6.97 per cent.

On distilling 100 grams of "*isocrotonic*" acid, about 40 grams boiled at  $87^\circ$  under 15—30 mm. pressure; the residue in the distilling flask became solid at the ordinary temperature, and the distillate was no purer than the original acid.

0.1773 gave 0.3515  $\text{CO}_2$  and 0.1190  $\text{H}_2\text{O}$ . C = 54.06; H = 7.45.

The analysis showed that it was not possible to purify the acid by further distillation. The liquid  $\beta$ -crotonic acid passed slowly into  $\alpha$ -crotonic acid and solidified completely.

*Brucine  $\beta$ -Crotonate.*—This salt is very soluble in water, alcohol, or benzene; from the last solvent, it crystallises out in prismatic needles, which melt between  $98^\circ$  and  $100^\circ$  without decomposition.

*Quinine  $\beta$ -Crotonate.*—The salt was prepared from the crude  $\beta$ -crotonic acid, and also from the acid which had been freshly distilled; the first crop of crystals melted at  $147^\circ$ , and on recrystallisation from water the fraction which separated first melted at  $156$ — $158^\circ$ , the melting point being unchanged on repeated crystallisation from this solvent. The mother liquors, from the crystallisation of the fraction melting at  $147^\circ$ , gave crystals which melted at  $134$ — $136^\circ$ . It would seem as if the two quinine salts crystallised together in about

equal quantities, and, on recrystallisation, separated into a less soluble form melting at 156—158° and a more soluble form melting at 134—136°.

$\beta$ -Crotonic acid, which had been distilled *in vacuo* at 87°, gave a quinine salt which melted at 147°. Seventy grams of the quinine salt (m. p. 147°), obtained from 30 grams of redistilled  $\beta$ -crotonic acid, gave, on recrystallisation, 60 grams of salt melting at 156°. The mother liquors were found to contain the quinine  $\alpha$ -crotonate (m. p. 132°). There is no evidence that quinine  $\beta$ -crotonate changes into the  $\alpha$ -salt on crystallisation from water. The quinine  $\beta$ -crotonate crystallises in prismatic needles; an air-dried specimen of the crystals, on heating at 105°, does not lose in weight. A determination of the solubility of the salt gave the following numbers: 13.5930 grams of a saturated aqueous solution at 17° contained 0.1410 gram of the salt, hence its solubility in water at 17° is 1.04.

0.3045 gave 18 c.c. moist nitrogen at 16° and 757 mm.  $N = 6.97$ .

0.1858 „ 0.4805  $CO_2$  and 0.1212  $H_2O$ .  $C = 70.5$ ;  $H = 7.24$ .

$C_{20}H_{24}O_2N_2 \cdot C_4H_6O_2$  requires  $C = 70.24$ ;  $H = 7.31$ ;  $N = 6.83$  per cent.

*Barium  $\beta$ -Crotonate.*—The quinine  $\beta$ -crotonate (m. p. 157°) was dissolved in hot water and decomposed by a slight excess of baryta water. The quinine was filtered off and a current of carbon dioxide passed through the filtrate in order to remove excess of baryta. The clear liquid was concentrated to a small bulk *in vacuo* at 50° and poured into alcohol; the barium salt was precipitated in large, lustrous, rhomboid plates, which contained a molecule of water of crystallisation.

0.9925 (air-dried) lost, at 110°, 0.0562  $H_2O$ .  $H_2O = 5.64$ .

0.2255 (dried at 110°) gave 0.1723  $BaSO_4$ .  $Ba = 44.85$ .

$(C_4H_5O_2)_2Ba \cdot H_2O$  requires  $H_2O = 5.53$ .  $(C_4H_5O_2)_2Ba$  requires  $Ba = 44.62$  per cent.

### *$\beta$ -Crotonic Acid.*

The barium  $\beta$ -crotonate was covered with pure ether and a little water added; the calculated quantity of 10 per cent. sulphuric acid was added drop by drop, the mixture being thoroughly shaken; the barium sulphate was removed by filtration and the clear ethereal solution of  $\beta$ -crotonic acid was concentrated *in vacuo* at the ordinary temperature. On cooling, the liquid acid solidifies immediately in long needles melting at 15°. Wislicenus gives the melting point of the acid as 15.5°; the melting point with the thermometer in the solid is 14—15°.

0.1856 gave 0.3765  $\text{CO}_2$  and 0.1161  $\text{H}_2\text{O}$ .  $\text{C} = 55.32$ ;  $\text{H} = 6.94$ .

0.1895 „ 0.3845  $\text{CO}_2$  „ 0.1180  $\text{H}_2\text{O}$ .  $\text{C} = 55.33$ ;  $\text{H} = 6.91$ .

$\text{C}_4\text{H}_6\text{O}_2$  requires  $\text{C} = 55.8$ ;  $\text{H} = 6.97$  per cent.

A molecular weight determination in glacial acetic acid gave the following numbers:

0.3903 in 16.7390 glacial acetic acid gave  $\Delta t = 1.062^\circ$ .  $\text{M. W.} = 85.6$ .

$\text{C}_4\text{H}_6\text{O}_2$  requires  $\text{M. W.} = 86$  per cent.

The density of the acid was found to be  $D_4^{25} = 1.0342$ ; Wislicenus (*loc. cit.*) obtained  $D_4^{15} = 1.0312$ .

Mr. Gold, of St. John's College, was kind enough to determine the refractive index of the acid for sodium light:  $\mu_D^{15} = 1.4483$ , molecular refraction = 37.27. The molecular refraction for  $\alpha$ -crotonic acid is 36.94 (Kannonikoff, *J. pr. Chem.*, 1885, [ii], 31, 347).

In order to test the purity of the  $\beta$ -crotonic acid obtained from the quinine salt, the following experiments were performed:

(a) 0.5 gram of the acid was dissolved in 7.5 c.c. of absolute alcohol and neutralised by a 10 per cent. absolute alcoholic solution of sodium hydroxide. The solution remained quite clear, which showed that the acid was free from  $\alpha$ -crotonic acid.

(b) Two grams of the acid were dissolved in 29.5 c.c. of absolute alcohol and the solution carefully neutralised by the alcoholic sodium hydroxide solution. An exceedingly slight precipitate formed, which was found to contain sodium carbonate. After filtration, the solution was evaporated to dryness, and the solid residue was extracted with 50 c.c. of absolute alcohol; the solid dissolved completely. From the alcoholic solution, the sodium  $\beta$ -crotonate was obtained, analysed, and its solubility in the solvent was determined.

0.255, dried at  $100^\circ$ , gave 0.1657  $\text{Na}_2\text{SO}_4$ .  $\text{Na} = 21$ .

$\text{C}_4\text{H}_5\text{O}_2\text{Na}$  requires  $\text{Na} = 21.3$  per cent.

4.759 grams of a saturated 99 per cent. alcoholic solution of sodium  $\beta$ -crotonate at  $15^\circ$  contained 0.3295 gram of the salt, therefore 1 part of the salt dissolves in 14.4 parts of 99 per cent. alcohol. Michael and Schulthess found that one part of the sodium  $\beta$ -crotonate dissolves in 16.7 parts of 99.5 per cent. alcohol at  $11^\circ$ , and in 12.7 parts of 98—99 per cent. alcohol at  $15^\circ$ .

#### *The Oxidation of Liquid $\beta$ -Crotonic Acid.*

“isoCrotonic” acid, obtained from Kahlbaum, was oxidised by barium permanganate according to the directions given by Fittig and Kochs (*Annalen*, 1892, 268, 16). The  $\alpha\beta$ -dihydroxybutyric acid was obtained as a syrup, although in one preparation some crystals appeared

in the form of long prisms with domed shaped ends, identical in appearance with those described by Fittig and Kochs (*loc. cit.*) as characteristic of  $\alpha\beta$ -dihydroxybutyric acid prepared from  $\alpha$ -crotonic acid. The yield of the syrup was the same as in the case of the oxidation of  $\alpha$ -crotonic acid. The brucine salt of this  $\alpha\beta$ -dihydroxybutyric acid is identical in melting point, specific rotatory power, and solubility with the  $\alpha\beta$ -dihydroxybutyric acid described in a former paper. Fractional crystallisation of the brucine salt gave a product melting at  $285^\circ$ , which amounted to more than 50 per cent. of the total weight of the salt taken. The "isocrotonic" acid contained so much of the  $\alpha$ -crotonic acid that it was found impossible to confirm Fittig and Koch's results. Investigation of the quinine salt gave the same results as in the case of the brucine salt. The proportion of quinine *cis*- $\alpha\beta$ -dihydroxybutyrate was at least 90 per cent. of the weight of the unrecrystallised quinine salt. The silver salt of this  $\alpha\beta$ -dihydroxybutyric acid was prepared, and its solubility compared with that of the silver *cis*- $\alpha\beta$ -dihydroxybutyrate. The solubilities at  $17^\circ$  were practically the same, being 3.2 and 3.1; the solubilities of the two  $\alpha\beta$ -dihydroxybutyrates at  $15^\circ$  and  $13^\circ$  are 1.45 and 5.1 respectively (Fittig and Kochs, *loc. cit.*).

## XL.—*Certain Organic Phosphorus Compounds.*

By AUGUSTUS EDWARD DIXON, M.D.

SOME few years ago, the author called attention to the existence of a kind of tautomerism, in which the mobility of hydrogen, or other monadic radicle, plays no part. The phenomenon, which takes the form of an apparent variability in the mode of attachment of a whole group, is observable amongst the so-called "thiocyanates" of organic acids, many of these exhibiting the power to interact, according to the conditions under which they are placed, either as such or as thiocarbimides (Trans., 1901, 79, 541). Following up the study of this peculiar behaviour, which seems to be confined exclusively to members of the class named,\* the writer was led to inquire whether a like

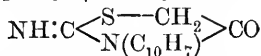
\* The isomeric rearrangement of a thiocyanate into a thiocarbimide is well known, for instance, that of allyl thiocyanate into the corresponding thiocarbamide, a change which occurs spontaneously on keeping. Amongst paraffinoid derivatives, the tendency to change is slight; nevertheless, a case has been observed, for Hofmann has recorded (*Ber.*, 1885, 18, 2197) the partial conversion of methyl thiocyanate into methylthiocarbimide by heating for several hours at a temperature of some  $50^\circ$  above the boiling point of the former. But these rearrangements are not

power would be manifested by the thiocyanates of mineral acid radicles, and some evidence was adduced (*loc. cit.*) to show that phosphorus and phosphoryl thiocyanates (which, however, were only obtained in solution) possess to a certain extent the characters of thiocarbimides. Since then, means have been found of isolating both these compounds with but little difficulty and the present paper includes a description of the methods employed, the properties of the products, and the results obtained by bringing them into contact with nitrogenous bases.

Before proceeding to the experimental data, it should, perhaps, be recalled that many new facts have lately come to our knowledge concerning the thiocyanates of organic radicles and their isomerides, the "mustard-oils," H. L. Wheeler having especially contributed in this direction. Amongst other things, it has now been established that double decomposition between metallic thiocyanates and halogen derivatives of substituted methanes does not necessarily lead to the formation of the corresponding thiocyanates, but that thiocarbimides are sometimes produced instead. Thus, potassium thiocyanate, when heated with phenyl-*p*-tolylmethyl bromide dissolved in benzene, yields the thiocarbimide,  $C_6H_4Me \cdot CHPh \cdot NCS$ , although benzyl-*p*-tolyl bromide is mainly converted into the corresponding thiocyanate (Wheeler and Jamieson, *J. Amer. Chem. Soc.*, 1902, 24, 746).

Phenyl- $\alpha$ -naphthylmethyl bromide and di- $\alpha$ -naphthylmethyl bromide under like treatment yield the thiocarbimides  $C_{10}H_7 \cdot CHPh \cdot NCS$  and  $(C_{10}H_7)_2CH \cdot NCS$  respectively. Diphenylmethyl bromide gives either  $Ph_2CH \cdot SCN$ , or  $Ph_2CH \cdot NCS$ , according to the conditions (Wheeler, *loc. cit.*, 1901, 26, 353), but ethyl phenyl- $\alpha$ -chloroacetate yields the thiocyno-derivative,  $CO_2Et \cdot CHPh \cdot SCN$ ; the latter, however, unites with aniline, giving rise to "diphenyl- $\psi$ -thiohydantoin,"  $PhN:C \begin{smallmatrix} S \cdot CHPh \\ NH-CO \end{smallmatrix}$ .

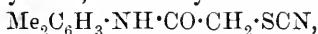
Further evidence of the tendency of thiocyanogen compounds to alter the character of their grouping is shown by the fact that chloroacetyl- $\alpha$ -naphthalide,  $CH_2Cl \cdot CO \cdot NH \cdot C_{10}H_7$ , gives, with potassium thiocyanate, a "labile  $\alpha$ -naphthyl- $\psi$ -thiohydantoin,"



(m. p. 147°), which changes, on boiling in dilute alcoholic solution, into the stable form,  $C_{10}H_7N:C \begin{smallmatrix} S-CH_2 \\ NH \cdot CO \end{smallmatrix} >$  (m. p. 213—214°). Moreover,

tautomeric in this sense, inasmuch as when once effected they are permanent; at least, conditions have not yet been discovered under which an alkyl thiocarbimide will behave as the thiocyanate of its own radicle. It may be noted incidentally that the  $\cdot NCS$  group, when once established, cannot be transferred by any known direct method from the radicle with which it is combined to another.

from chloroacetyl-*m*-xylidide, the thiocyano-derivative,



can be isolated, which readily undergoes isomeric change into the stable form of thiohydantoin (Johnson, *loc. cit.*, 1903, 25, 483). It may be added here that the formulæ given by Wheeler and others for the stable varieties confirm those previously advanced (Dixon, *Trans.*, 1897, 71, 629) for the ordinary so-called thiohydantoins. The present writer observed many years ago that chloroacetanilide, when heated in dilute alcohol with potassium thiocyanate, yields not only phenylthiohydantoic acid, but, in addition, a considerable proportion (62 per cent. of the theoretical) of phenylthiohydantoin, a substance which is also produced either from chloroacetanilide and thiocarbamide, or from phenylthiocarbamide and ethyl chloroacetate (Meyer, *Ber.*, 1877, 10, 1965). However, the fact that this substance results indifferently from compounds containing thiocyano- or thiocarbimino-groups does not conclusively prove that the former radicle changes into the latter. Another interesting action, which shows the power of the  $\cdot\text{SCN}$  radicle to combine occasionally with a base, is the union of 1 mol. of aniline with trimethylene thiocyanate, thereby forming phenyl- $\psi$ -trimethylenedithiobiuret,  $\text{CH}_2\left\langle\begin{smallmatrix}\text{CH}_2\cdot\text{S}\cdot\text{C}(\text{NH}) \\ \text{CH}_2\cdot\text{S}\cdot\text{C}(\text{NH})\end{smallmatrix}\right\rangle\text{NPh}$  (Wheeler and Merriam, *loc. cit.*, 1902, 24, 446).

The case of acidic thiocyanates is somewhat complex. Since the electro-positive character of the unsaturated hydrocarbon groups is commonly less marked than that of the saturated, it might be anticipated that the thiocyanates of pronounced electro-negative radicles would tend still more readily to pass into the thiocarbimidic form, and to some extent this is true, for the derivatives of benzenoid acids exhibit mainly (although not exclusively) the properties of thiocarbimides; in fact, Miquel, the discoverer of benzoyl "thiocyanate" (*Ann. chim. phys.*, 1877, [v], 11, 300), states that if pure it is hydrolysed by water into benzamide and carbon oxysulphide, but yields no thiocyanic acid, and hence ought to be regarded as a true thiocarbimide.

Now, the substance in question, when formed by heating benzoyl chloride dissolved in benzene with lead thiocyanate for a few minutes, may give, by combination with alcohols or nitrogenous bases, yields of the corresponding additive products amounting to fully 90 per cent. of the theoretical (compare *Trans.*, 1896, 69, 1603; 1899, 79, 379), and hence if benzoyl thiocyanate is formed at all in the initial decomposition, which necessarily occurs at a very moderate temperature, its existence as such is short.

On the other hand, thiocyanates derived from certain fatty acids appear capable of exhibiting the kind of tautomerism previously men-

tioned, with respect to the CNS group : stearyl thiocyanate, for example, gave (*loc. cit.*, 1602) with benzylaniline more than 95 per cent. of the possible yield of the trisubstituted thiocarbamide, whilst with ammonia the products were substantially thiocyanic acid and stearamide.

Occasionally, a substance of this class can not only act separately in either form, but also simultaneously in both : acetyl thiocyanate, for instance, is decomposed by water (Miquel, *loc. cit.*), mainly into acetic and thiocyanic acids ; it can unite almost quantitatively with *p*-toluidine to form acetyl-*p*-tolylthiocarbamide ; whilst if brought into contact with aniline at the ordinary temperature, it yields acetylphenylthiocarbamide and acetanilide, together with aniline thiocyanate. In relation to aniline, Doran's observation has already been mentioned, that the power of acetyl thiocyanate to behave either as such, or as acetylthiocarbimide, is conditioned mainly by the temperature at which the interaction is brought about (*Trans.*, 1901, 79, 543 ; *Proc.*, 1904, 20, 20).\*

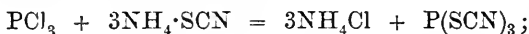
If any analogy may be looked for between the thiocyanates of electro-negative organic, and of electro-negative mineral radicles, it would presumably take the form of a similar capacity, on the part of members of the latter class, to manifest thiocarbimide in addition to thiocyanic functions ; or possibly, under certain conditions, to act as thiocarbimides, pure and simple. No investigation from this point of view seems as yet to have been conducted, excepting a superficial one by the writer. The present study, indeed, notwithstanding that upwards of two years have been devoted to it, has scarcely passed the preliminary stage, but circumstances having arisen which will for some little time interfere with the prosecution of this research, an account of the principal results so far attained is now submitted.

### *Phosphorus "Trithiocyanate."*

Phosphorus trichloride interacts spontaneously with dry ammonium thiocyanate ; the violence of the direct action may be suitably checked by mixing the finely-powdered thiocyanate with enough benzene to make a thin paste, and then adding the phosphorus halide diluted with three or four times its own volume of the same solvent. The mixture instantly becomes hot, and must be kept in rapid motion for a short

\* The behaviour of these substances is sometimes very puzzling. For instance, propionylthiocarbimide and benzylaniline gave (*Trans.*, 1896, 69, 859) nearly 90 per cent. of the possible yield of propionylphenylbenzylthiocarbamide, but with piperidine it afforded piperidine thiocyanate. In another experiment, sodium ethoxide was added to the acetyl compound, dissolved in benzene, in the hope of realising the change,  $\text{NaOEt} + \text{AcNCS} = \text{NaOAc} + \text{EtNCS}$  ; vigorous action occurred, the products being sodium thiocyanate and ethyl acetate, but not a trace of ethylthiocarbimide could be detected.

time, otherwise a portion of the contents may be projected out of the flask. It is well to use about one and a half times the amount of thiocyanate calculated from the equation,



if the process is successfully conducted, there is but little change of colour, and in a few minutes the benzene solution becomes practically free from chlorine. By using dilute solutions, all danger of violent action is precluded, but it may then be necessary either to allow the mixture to remain for about a day, or to boil in order to eliminate the chlorine, and in these circumstances a yellow or bright orange-coloured solid develops, which appears to consist mainly of pseudo-sulphocyanogen together with isoperthiocyanic acid. When cool, the residue of ammonium chloride and thiocyanate is filtered off at the pump, washed a few times with dry benzene, and the clear filtrate heated on the water-bath under reduced pressure until no more solvent can be extracted. On distilling the pale brown liquid thus obtained *in vacuo*, the thermometer rose quickly to about  $168^\circ$ , when a few drops of liquid passed over; the contents of the flask now became very dark and semi-solid, and from this product, by careful heating, a clear, pale yellow oil could be distilled, the whole distillate usually passing over within one or two degrees. In various preparations, the following boiling points and pressures were observed:  $170^\circ/20$  mm.;  $172^\circ/21$  mm.;  $173^\circ$  and  $175^\circ/27$  mm.;  $175^\circ/28$  mm., and  $180^\circ/30$  mm. On rectification, two specimens were obtained boiling at  $169^\circ/20$  mm. and at  $161^\circ/14$  mm. respectively; the latter sample, when again rectified, boiled at  $163^\circ/15$  mm.; in all cases, a considerable amount of dark, viscid residue was left. These figures are mentioned in detail, because, although they seem to indicate a perfectly definite compound, reasons will be assigned later on for doubting whether the product is really homogeneous.

The distillation is rather troublesome, being attended with much spirting and frothing of the viscid paste, and the slight irregularities noticeable in the boiling points are perhaps due to the projection of liquid drops against the bulb of the thermometer.

The best yield, from 14 grams of trichloride, was only 41 per cent. of the theoretical. The smaller yields obtained from larger batches were probably due to the decomposition of the substance caused by prolonged exposure at the somewhat high temperature.

Potassium thiocyanate interacts very imperfectly with phosphorus trichloride (compare Trans., 1901, 79, 545), and although the corresponding lead salt acts well enough, the mixture sometimes requires prolonged boiling in order to complete the change.

When exposed to air, the distilled oil slowly evolves fumes of thio-

cyanic acid, but does not spontaneously inflame, even on warming. In the cold, it has a faint alliaceous odour, which becomes penetrating and exceedingly disagreeable on heating the oil with water; this mixture is not luminous in a darkened room; even when very slightly impure, the liquid soon darkens and becomes turbid. A specimen, when thrice distilled, was found to have a sp. gr. 1.487 at 15.5°; this figure differs considerably from that given by Miquel (*loc. cit.*), who found a sp. gr. 1.625 at 18° for a product distilled under the ordinary pressure. In relation to solvents, it corresponded with his description in all respects, except one, which will be mentioned later.

Analysis gave: S = 46.9; N = 20.1; P = 15.0.

$C_3N_3S_3P$  requires S = 46.83; N = 20.48; P = 15.12 per cent.

When thrown into water, the oil at once commences to dissolve, but does not entirely disappear, the solution containing thiocyanic and phosphorous acids. These, however, are not the only products, for if it is mixed with silver nitrate and the precipitated silver thiocyanate dissolved by ammonia, the liquid remains dark and turbid, owing to the presence of a little silver sulphide; moreover, if it is heated with alkaline solution of lead salts, very perceptible desulphurisation occurs. Consequently, although the oil behaves mainly as a thiocyanate in so far as the aqueous extract is concerned, the latter also gives to some extent the reactions of a thiocarbimide. On the other hand, if the oil is dropped into hot alkaline solutions of lead or silver salts, copious desulphurisation occurs instantly, the substance thus exhibiting in a marked degree the characters of a thiocarbimide.

On mixing the oil (1 mol.) and aniline (3 mols.) in warm benzene, much heat was developed and a tenacious oil separated; after prolonged exposure to air, this became partly crystallised, but when the oil was removed by means of acetone, the crystalline residue proved to be merely phenylthiocarbamide. With cooled solutions, a pasty, amorphous solid was obtained, which hardened when kept out of contact with moisture, but which, when powdered and washed successively with benzene and light petroleum, still retained a trace of viscid matter; it softened at about 67° and melted somewhat indefinitely two degrees higher. The yellow powder contained a little aniline thiocyanate, for if shaken with water, in which it was practically insoluble, the liquid was distinctly reddened by ferric chloride, and gave with bleaching powder the violet reaction for aniline. When heated with water, it dissolved readily, a little hydrogen sulphide being evolved; the solution reacted freely for thiocyanic and phosphorous acids and for aniline, and deposited phenylthiocarbamide on cooling. It was easily soluble in ether, alcohol, and some other solvents, but when recovered from solution, either by evaporation or by precipitation, it always separated

either as a liquid or a paste. The indefinite melting point was suggestive of an impure compound, but as no satisfactory method of purification could be devised, the well-washed crude product was partially analysed, with the following results:

Found, S = 21.3; N = 16.5; P = 6.2.

These figures agree only indifferently with the composition  $P(SCN)_3 \cdot 3C_6H_5 \cdot NH_2$  or  $C_{21}H_{21}N_6S_3P$ , which would require S = 19.83; N = 17.35; P = 6.4 per cent.

*o*-Toluidine, when employed in a similar manner, yielded a smeary brown oil, from which only *o*-tolylthiocarbamide could be extracted. The distilled oil was soluble in alcohol, with which it interacted at once, considerable heat being developed; thiocyanic acid escaped, and a viscid paste was left which did not crystallise or become solid even after two months.

It has already been mentioned that in one respect the phosphorus thiocyanate did not correspond with Miquel's description. According to this author, the substance is but very slowly acted on by water, which decomposes it into thiocyanic and phosphorous acids. This was not exactly the present writer's experience, for cold water attacked the oil rapidly, the solution obtained by shaking the two together for a few seconds containing a large amount of thiocyanic acid. Yet, on attempting to determine quantitatively the amount of this acid, it was found that, although the oil rapidly diminished in bulk when first placed in contact with warm water, it could not be made to dissolve completely, even by prolonged boiling, nor did the substitution of fresh water for that now charged with the decomposition products appear to diminish the amount of residual oil; moreover, the latter, after repeated extractions, ceased to afford any reaction for thiocyanic acid, even if kept for several hours in contact with water, but it was copiously desulphurised by alkaline lead or silver salts. In fact, the liquid was now apparently free from phosphorus thiocyanate, although it still displayed the characteristic properties of a true thiocarbimide.

In order to ascertain the nature of this residual oil, experiments were now conducted on a larger scale: 16.4 grams of freshly distilled oil were shaken with successive amounts of about 50 c.c. of hot water and then repeatedly boiled with this solvent; the aqueous portions at first contained large quantities of phosphorous and thiocyanic acids, but after some fifteen extractions, the cold aqueous extract no longer developed any red coloration with ferric chloride. Cold water was used in this experiment, because it was found that, no matter how often the treatment with boiling water was performed, a trace of ferric thiocyanate always appeared. After a few additional extractions, the residual oil was drawn off, its amount in this experi-

ment being 54 per cent. of the weight initially taken. In another experiment with thrice-distilled oil, the yield was 65 per cent. When dried over calcium chloride, the oil was distilled under reduced pressure, the boiling points observed being  $173-174^{\circ}$  and  $168^{\circ}$  under 22 mm. and 17 mm. pressure respectively; distillation now occurred with much less bumping than before, the contents of the flask did not solidify or even thicken, and the amount of dark-coloured residue was very small. It will be noted that the former boiling point lies very close to that observed for an unwashed specimen, whilst the latter is not very far removed from the mean of  $163^{\circ}$  and  $169^{\circ}$  under 15 and 20 mm. pressure respectively, observed on rectifying the unwashed products.

The distillate was a clear, colourless, highly refractive oil; the sp. gr. of the two specimens were 1.483 and 1.488 at  $16^{\circ}$ , whilst that of the unwashed oil, as mentioned above, was 1.487 at  $15.5^{\circ}$ . Considering that only 2 to 5 c.c. of liquid were used in the determinations, these figures are practically identical; in other words, the removal, by washing, of from about one-half to one-third of the substance of the oil did not materially affect either its specific gravity or its boiling point. These facts are consistent with the view that the oil is a homogeneous compound; for, if only slowly soluble in water, a portion might be withdrawn, leaving a residue with properties unchanged, but this refers to the physical properties alone, and does not explain why hydrolysis no longer occurs after some extractions, or why water dissolves only a portion of the oil.

On examining the distillate, it was found to undergo copious desulphurisation when warmed with alkaline solutions of lead salts or when its alcoholic solution was mixed with ammoniacal silver nitrate. But when shaken with water, the aqueous portion gave not a trace of red coloration with ferric chloride, and hence, not only was the phosphorus trithiocyanate (assuming that to be the source of the thiocyanic acid produced by contact with water) completely removed by washing, but, moreover, the residual portion did not regain the power to behave as a thiocyanate after having been subjected to a moderately high temperature. Excepting that it was practically insoluble in water, the new substance had properties very similar to those of the unwashed material, and when analysed gave the following results:

Found, S = 47.2. N = 20.9; P = 15.2.

$C_3N_3S_3P$  requires S = 46.83. N = 20.49; P = 15.12 per cent.

Now if true phosphorus trithiocyanate is hydrolysed by contact with water, the liquid isolated by the foregoing method must be an isomeride, and hence, presumably, the hitherto unknown phosphorus

trithiocarbimide. Obviously, the next step was to ascertain whether it possessed the characteristic property of uniting with a primary nitrogenous base so as to yield the corresponding thiocarbamide.

In order to test this point, a benzene solution of aniline was slowly added from a burette to a weighed quantity of the pure oil, freely diluted with this solvent, and kept near the freezing point of the mixture. A finely-divided white solid at once began to separate, and the addition of the aniline was continued until a portion of the filtered liquid, when treated with a few drops of the solution, just ceased to yield any further precipitate, this stage being reached when, for each mol. of the oil taken, one mol. of aniline had been used. Excess of base was avoided, because it readily combines with the solid product, turning it into a viscid paste. The white powder was filtered off and washed thoroughly with dry benzene; on allowing the filtrate to evaporate, there was scarcely any residue, thus showing that the aniline had almost completely removed the dissolved oil; the solid product, when dry, amounted to nearly 98 per cent. of the total weight of materials used.

When heated in a narrow tube, the substance melted sharply without effervescence at  $116-117^{\circ}$  (corr.), changing into a golden-yellow liquid.

Found,  $S = 32.1$ .  $N = 18.2$ ;  $P = 10.25$ .

$C_9H_7N_4S_3P$  requires  $S = 32.21$ ;  $N = 18.79$ ;  $P = 10.40$  per cent.

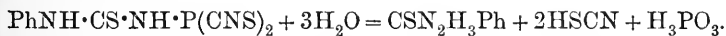
Accordingly, the product was a definite additive compound,  $P(CNS)_3 \cdot C_6H_5 \cdot NH_2$ . Cold water had practically no effect on it excepting after prolonged contact, but if warmed on the water-bath the mixture gradually became clear, a little hydrogen sulphide being evolved; when this was boiled off, the solution contained a large amount of thiocyanic acid, and was freely desulphurised by heating with alkaline lead tartrate. The source of the desulphurisation was phenylthiocarbamide, which separated in large crystals as the liquid cooled; only a trace of aniline could be detected and the solution, when oxidised by nitric acid, gave the reactions of phosphoric acid with magnesia mixture and with ammonium molybdate.

It is curious to note that, whilst the parent oil is scarcely affected by water, even at the boiling point, yet after union with 1 mol. of aniline the resultant compound is easily hydrolysed, the uncombined CNS groups when thus separated making their appearance mainly as thiocyanic acid, although a little hydrogen sulphide is also formed. In order to follow more clearly the course of the hydrolysis, some quantitative experiments were carried out, a few of which may be mentioned.

To determine the amount of hydrogen sulphide liberated, a weighed

quantity of the solid was digested on the water-bath for half an hour with excess of arsenious acid solution slightly acidified with hydrochloric acid; the arsenious sulphide was collected, washed, dissolved by boiling for some hours with water, and the arsenic estimated by standard iodine; the sulphur thus precipitated amounted to about 4 per cent. Then, by boiling a weighed quantity with water, allowing to cool, and collecting the phenylthiocarbamide formed, it was found that six-sevenths of one-third of the total sulphur, or 9.2 per cent., came out in this form, instead of 10.7. The solution of a weighed quantity, hydrolysed by water alone, was next treated with excess of silver nitrate, the mixed sulphide and thiocyanate separated by means of ammonia, and the latter salt, after precipitation with dilute nitric acid, collected, dried at 110°, and weighed; the mean of three fairly concordant determinations was 18 per cent. of sulphur in the form of thiocyanic acid, thus accounting for 97 per cent. of the total sulphur. The last result was checked in another way, by colorimetric estimation with a ferric salt, using *N*/400 potassium thiocyanate as standard; although this process is not very accurate, it was thus found that approximately two-thirds of the sulphur were hydrolysed to thiocyanic acid.

Neglecting the formation of the hydrogen sulphide, the hydrolysis takes the following course: one  $\cdot\text{NCS}$  radicle is eliminated with the aniline residue as phenylthiocarbamide, and the two remaining  $\text{CNS}$  groups appear as thiocyanic acid; these results may be summed up by the equation:



Assuming, for the moment, that the parent compound is wholly thiocarbimide as to the contained  $\text{CNS}$ , it may appear strange that of the three  $\cdot\text{NCS}$  groups one alone should exhibit pronounced activity in uniting with aniline, but so far as this is concerned the case is not without a parallel, the author having already observed a similar peculiarity with carbonyldithiocarbimide,  $\text{CO}(\text{NCS})_2$ ; this substance, when treated with aniline until the precipitation of solid matter was just complete, gave carbonylthiocarbimidophenylthiocarbamide,  $\text{SCN}\cdot\text{CO}\cdot\text{NH}\cdot\text{CS}\cdot\text{NHPh}$  (*Trans.*, 1903, 83, 89). In this case, it was found possible, by allowing the thiocarbimide to remain for a day or so in contact with excess of base, to obtain the dithiocarbamide,  $\text{CO}(\text{NH}\cdot\text{CS}\cdot\text{NHPh})_2$ , but with benzyaniline only 1 mol. could thus be added. From these few data, it would be unsafe to generalise; nevertheless, so far as they go, they tend to indicate that, as  $\cdot\text{NCS}$  groups accumulate in the acid molecule, their characteristic power of uniting with primary and secondary nitrogenous bases to yield thiocarbamides becomes weakened. This may be equally true for certain combinations with inorganic radicles, and, if so, when a single phos-

phorus atom is united with three supposed thiocarbimidic radicles, the fact that one alone is capable of readily discharging the function peculiar to these groups, although no more intelligible than before, is nevertheless not quite abnormal.

Without making assumptions with regard to the nature of the contained CNS groups, it is convenient to call that portion of the phosphoretted oil which is removed and hydrolysed by water, "phosphorus thiocyanate," and that fraction which is not, "phosphorus thiocarbimide." The monophenylthiocarbamidic derivative of phosphorus thiocarbimide, when suspended in warm benzene and mixed with 2 mols. of aniline, united with the latter quantitatively, forming a viscid oil, which slowly hardened ; after powdering and washing with benzene, the ill-defined product resembled that obtained by the direct action of 3 mois. of aniline on one of the unwashed distillate, and when treated with hot water, underwent hydrolysis, yielding much aniline thiocyanate, together with phenylthiocarbamide.

Found, S = 19.7 ; P = 5.9 ;  $P(CNS)_3, 3PhNH_2$  requires 19.83 and 6.4 per cent.

That the further quantity of aniline taken up by the monophenyl compound had not entered into true thiocarbamidic combination, was made evident by the result of hydrolysis, when only 30 per cent. of the total sulphur made its appearance in the form of phenylthiocarbamide.

It has been stated above that phosphorus trithiocarbimide is not attacked by water, and this is practically true. But if the oil, repeatedly washed with boiling water until the residue, when vigorously shaken with the cold or tepid solvent, does not cause the latter to give the slightest coloration with ferric chloride, is now left in contact with cold water, thiocyanic acid slowly passes into solution, so that after a few days the colour reaction may again be produced. A few washings with hot water suffice to remove all trace of the acid, but on leaving the residue with a fresh quantity of water for two or three days, thiocyanic acid can be found in solution, just as before : a sample of washed and distilled oil, thus treated nine times at intervals of five or six days, had in the end become perceptibly reduced in bulk, but the residual oil, when thoroughly washed with boiling water and then left in contact with the cold solvent, gave the reaction apparently as markedly as at the beginning. When left for six months, with occasional changes of water, the oil had not disappeared, and what was left did not seem changed, except in amount. The solution, if decidedly reddened by ferric chloride, always gave a slight, but distinct, desulphurisation when heated with alkaline lead or silver

salts; it is therefore probable that the "phosphorus thiocarbimide" slowly dissolves in the water as such, but cannot accumulate to any appreciable extent, because the solution soon undergoes hydrolysis. If the aqueous mixture is kept for a month, it still gives only a slight desulphurisation when freed from the oil, whilst the thiocyanic reaction has now become strongly marked.

Sharply contrasted with this reversion, which is so slow and minimal that it might easily escape notice, is the copious and rapid production of thiocyanic acid, which occurs on dissolving the monophenyl compound in warm water; a possible explanation is that, when once the molecule is broken by the splitting off of the group  $\cdot\text{NH}\cdot\text{CS}\cdot\text{NHPh}$  (representing it as symmetrical), the residue becomes unstable, and decomposes forthwith into thiocyanic and phosphorous acids.

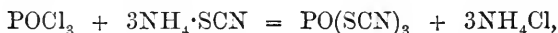
It is not easy, from the facts at present available, to understand the precise nature of the distillate first obtained from phosphorus trichloride and ammonium thiocyanate before its thiocyanic characters (with respect to water) have been practically destroyed by washing. The view that phosphorus trithiocarbimide is first formed and then decomposes partially into trithiocyanate is contrary to experience with other thiocarbimides, and is further negatived by the fact that when the trithiocarbimide has once been freed from thiocyanate, it does not afford a trace of the latter on redistillation. On the other hand, the converse assumption is not without some basis, for whilst a specimen, only once distilled, but apparently pure, judging from the analytical results, lost only about half its weight on treatment with water, another, thrice distilled, lost only about one-third. However, the preparations were not always made under precisely identical conditions as regards temperature, time, dilution, &c., so that this argument should not be pressed too far; and the direct evidence cannot yet be obtained, namely, that pure "phosphorus thiocyanate" is able to change at all into the thiocarbimide, since no means is known whereby the former can be isolated.

It might seem obvious, at first sight, that "phosphorus thiocyanate," which is acted on readily by water, must be a substance chemically distinct from "phosphorus thiocarbimide," which is not; but as the presence of much thiocyanate has scarcely any perceptible effect on either the density or the boiling point of the latter, there can be but little dissimilarity between them in respect of these physical properties. So far as the present experiments have gone, the washed oil appears to have a slightly higher boiling point than the unwashed, but the difference, if it exists, cannot exceed some two or three degrees within the limits of pressure specified. Amongst hydrocarbon derivatives, the thiocyanate of a given radicle boils, on the average,

some 11 or 12° above the thiocarbimide,\* so that, unless the difference is very small in the case of acid derivatives, the only reason for supposing the original distilled oil to be a mixture of two distinct substances lies in the fact that the rate of attack by water undergoes great retardation as the process of washing is continued. As regards the power to unite with one or three mols. of base, it does not appear to matter whether the "thiocyanate" is removed or not; moreover, it will presently be shown that a phosphoryl derivative, not washed, gives additive products precisely similar to those obtained with the washed phosphorus "trithiocarbimide."

*Phosphoryl "Thiocyanate."*

When phosphoryl chloride, diluted with dry benzene or toluene, was allowed to remain in contact with about one and a half times the amount of carefully-dried potassium or ammonium thiocyanate required according to the equation:



interaction took place spontaneously: the mixture was then separated by means of the pump into (1) a solid residue, and (2) a clear yellow filtrate, no longer smelling of oxychloride. When treated with cold water, this residue yielded chloride and unchanged thiocyanate, leaving a yellow, amorphous powder, mostly soluble in boiling water, and giving the reactions of *isoperthiocyanic* acid. The filtrate was heated on the steam-bath, under reduced pressure, until the solvent was eliminated, and the residue, a viscid, reddish-yellow syrup, was submitted to distillation in a vacuum. The clear, pale yellow, highly refractive oil thus obtained boiled at 175° (uncorr.) under 21 mm. pressure; it had a faintly pungent odour, and slowly evolved fumes of thiocyanic acid when exposed to ordinary moist air. If tolerably pure, it may be kept for weeks without material alteration, otherwise it quickly becomes turbid, depositing a red, pasty substance.

The yield of distilled product was not very satisfactory, the best attained being only 43 per cent. of the calculated quantity. As the crude oil bumps and froths considerably, a relatively large flask must be used, and the amount of material taken should not be large, for when the distillation is much retarded a good deal of black tar accumulates, which apparently is formed from the oil by prolonged heating at the boiling temperature.

A freshly distilled specimen was analysed, with the following results:

\* The difference in specific gravity is usually inconsiderable for each pair of isomerides.

Found, N = 19.15 ; S = 43.7 ; P = 14.2.

$C_3N_3S_3OP$  requires N = 19.02 ; S = 43.45 ; P = 14.02 per cent.

The sp. gr. is 1.52 at 13.5°.

When mixed with excess of cold water, the oil dissolved, undergoing hydrolysis tolerably rapidly; the solution gave with ferric chloride a deep blood-red coloration, and with ammonium molybdate or magnesia mixture the reactions of phosphoric acid. The change under these conditions is mainly that represented by the equation:  $PO(SCN)_3 + 3H_2O = 3HSCN + H_3PO_4$ , for a dilute solution, when treated successively with excess of ammonia and silver nitrate, became only slightly darkened, and was not markedly desulphurised by boiling with alkaline lead tartrate. Moreover, about half a gram of the fresh oil, when decomposed by cold water, and treated with ammonia and magnesia mixture, yielded a quantitative amount of phosphoric acid, as calculated from the above equation.

So far, therefore, the substance displays mainly the properties of a thiocyanate, but when added directly to and shaken with an alkaline solution of lead tartrate, a white precipitate was formed, which slowly became yellow and orange, and finally black; this change, which is due to the production of lead sulphide, occurred instantly on gently warming, and the alcoholic solution, when mixed with silver nitrate and ammonia, was abundantly desulphurised, even in the cold; in these circumstances, the substance exhibited markedly the characters of a thiocarbimide.

In the case of the phosphoryl compound, it was not found possible to eliminate the thiocyanate, leaving a thiocarbimidic residue, for on shaking 5 grams of the oil with about 20 c.c. of cold water, heat was developed, and the whole of the oil, except a decigram or so, rapidly dissolved, and when left for some little time, a yellow solid appeared, which was found to consist principally of *isoperthiocyanic acid*; with 14 grams of oil, a similar result was obtained.

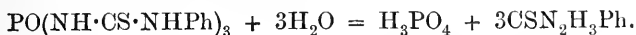
Since a thiocarbimide, as such, could not be isolated, an attempt was made to combine the oil with organic amines, so as to obtain substituted thiocarbamides, but the experimental difficulties are very great, for, although combination occurs readily enough, the products are very unsatisfactory. Even when formed from apparently pure materials, they are often far from pure, and although usually presenting the appearance of crystallisable compounds, they have, so far, resisted every attempt made in this direction. By contact with water or with solvents containing even traces of it, they are readily hydrolysed, so that, after many failures and in the absence of any better method, carefully purified materials were used for the preparations; the products were thoroughly washed successively with benzene and

light petroleum, dried at the ordinary temperature as far as possible in the absence of moisture, and then analysed.

It will be seen from what follows that phosphoryl thiocyanate is capable of fixing primary amines, of which 1 mol. is held for each SCN group present, and this, without the formation of basic thiocyanate; nevertheless, the products are not true thiocarbamides (or, if so, differ from those at present recognised), since, when hydrolysed, they yield, not thiocarbamide alone, but a mixture of thiocarbamide with basic thiocyanate. The results obtained in the experiments were not invariably the same, although approximately so; each account given below is that of observations actually made, and not the average of a number of experiments.

*Action of Aniline.*—Eight grams of the oil were mixed with three molecular proportions of aniline, each reagent being diluted with about twice its volume of dry benzene; interaction occurred instantly, the temperature rising to the boiling point of the mixture, and a yellow, doughy paste separated, which quickly became hard, and, when broken up and dried, formed a mobile powder, the weight of which approximately equalled that of the materials taken. The substance had no definite melting point; it became translucent at 89° and frothed at 95—97°. When added to water, it was apparently quite insoluble, the mixture, even after thorough shaking, being neutral to litmus, and giving no reaction with ferric chloride or with calcium hypochlorite solution; consequently, the powder was free from aniline thiocyanate. When left for an hour or so with cold water, the mixture began to give the red thiocyanate coloration with ferric chloride, which slowly increased with the time. But if boiled with water, the solid quickly dissolved, evolving a little hydrogen sulphide and leaving a trace of viscid oil; the solution now obtained was intensely acid, contained large amounts of aniline, thiocyanate, and phosphoric acid, and on cooling deposited large crystals of phenylthiocarbamide. The production of the latter is not due to isomeric change of the aniline thiocyanate through heating, for the original solid, when dissolved in cold spirit, is desulphurised by ammoniacal silver nitrate; moreover, if it is dissolved in cold dilute aqueous caustic potash and treated with a lead salt, a white precipitate is formed, becoming successively yellow, orange, brown, and finally jet-black; the last change occurs at once on gently warming. It is unnecessary to describe in further detail the properties of this compound, for they agreed in every respect with those observed for the product obtained from the cumene solution, supposed to contain phosphoryl thiocyanate (Trans., 1901, 79, 549). Concerning the last-named product, it was mentioned (*loc. cit.*) that when hydrolysed with boiling water it

yielded barely one-third of the phenylthiocarbamide which should be formed according to the equation :



Whether the limited production of phenylthiocarbamide was normal or otherwise could not then be decided, since it was uncertain whether the cumene solution contained one substance only. This time, however, there could be little doubt as to the chemical individuality of the oil, seeing that, apart from the analytical figures, the whole 8 grams of product distilled within about  $1^\circ$ .

In repeating the experiment, 5 grams of the aniline compound were dissolved in 50 c.c. of boiling water, and the solution filtered from a trace of viscid oil ; on cooling, pure phenylthiocarbamide was deposited, the weight being 1.4 grams, corresponding with 28 per cent. of the theoretical as reckoned above ; in another experiment, 30 per cent. was obtained. A further small quantity remained in solution, but this could not safely be collected by evaporation to a small bulk, because the aniline thiocyanate present gradually changes, under the influence of heat, into phenylthiocarbamide. This result, seeing that the experiment was only a rough one, does not differ materially from that previously recorded. Although the substance used had been well washed with benzene, it was evidently not quite pure, as shown by the ill-defined melting point, and by its failure to dissolve perfectly in water ; an estimation of sulphur gave 18.9 per cent. against 19.21 calculated for  $\text{C}_{21}\text{H}_{21}\text{N}_6\text{OS}_3\text{P}$ , and the nitrogen was also too low ; the phosphorus, however, was found = 6.5, the calculated number being 6.45 per cent.

Until the methods and results now given can be improved, it may provisionally be concluded that phosphoryl thiocyanate is a definite chemical compound, which, when in contact with water, behaves as a true thiocyanate, but in presence of benzene alone can quantitatively fix three molecules of aniline, thus behaving as a typical (tri)thiocarbimide ; the product, although free from aniline thiocyanate, can, nevertheless, readily yield it by hydrolysis, together with a little hydrogen sulphide, somewhat less than one-third of the contained sulphur being simultaneously liberated in the form of phenylthiocarbamide. Of the three CNS groups present in the molecule, it appears, therefore, that only one is capable of exerting the power peculiar to the thiocarbimidic residue,  $\cdot\text{NCS}$ , of uniting with an amine so as to yield an atomic complex devoid of thiocyanic characters ; the two remaining groups, when once the former is saturated, appear to be thiocyanic in nature, although possessing a certain capacity to hold the base in combination.

It is possible to bring about union between the thiocarbimidic group alone and aniline, leaving the other two groups uncombined, as shown by the following experiment.

To a cooled solution containing 1 mol. of freshly distilled oil in about ten times its volume of benzene, 1 mol. of aniline was very slowly added with constant stirring; a minutely-divided, white, amorphous solid was precipitated, the liquor from which gave no further precipitate with aniline, and left scarcely any residue on evaporation; the solid, when thoroughly washed successively with benzene and light petroleum and dried by gently heating, was equal to 93 per cent. of the total weight of materials combined. Had the aniline combined equally with all the SCN groups, much thiocyanate must have been left, whilst the yield of solid could not have exceeded 53 per cent. of the total weight of the reagents.

The powder softened at  $119^{\circ}$  and melted at  $120\text{--}121^{\circ}$  (corr.); it was insoluble, or nearly so, in cold water, the mixture giving a feeble reaction for thiocyanic acid, but, on warming, it soon dissolved, the solution being highly acid, and containing free phosphoric and thiocyanic acids, together with phenylthiocarbamide. As usual, a trace of hydrogen sulphide was evolved, but the solution gave only a faint reaction for aniline.

Analyses gave:  $S = 30.3$ ;  $P = 9.95$ .

$C_9H_7N_4OS_3P$  requires  $S = 30.6$ ;  $P = 9.87$  per cent.

The phenylthiocarbamide produced by hydrolysis was collected and dried at  $100^{\circ}$ ; it amounted, as in the case of the phosphorous analogue, to six-sevenths of that which could be formed according to the equation:  $PhNH \cdot CS \cdot NH \cdot PO(CNS)_2 + 3H_2O = CSN_2H_3Ph + H_3PO_4 + 2HSCN$ .

When the above monophenyl compound (1 mol.) was suspended in benzene and warmed on the water-bath with aniline (2 mols.), combination occurred, a clear, brown oil being formed, which hardened to a brittle resin on cooling, the latter, when powdered, washed with benzene, and dried, amounting to 96 per cent. of the weight of materials taken; it resembled in all respects the product obtained by treating the trithiocyanate directly with 3 mols. of aniline, and gave, on analysis,  $N = 17.3$  and  $S = 18.8$  per cent., the calculated values being  $N = 16.84$  and  $S = 19.21$  for  $PO(SCN)_3, 3C_6H_5NH_2$ .

A portion, hydrolysed by warming with water for three-quarters of an hour, yielded 41 per cent. of its sulphur in the form of phenylthiocarbamide; this unusually high percentage is probably due to the transformation of a portion of the aniline thiocyanate due to prolonged heating.

*Action of p-Toluidine* (3 mols.).—When brought into contact with one

another in warm dilute benzene solution, the reagents united vigorously, the mixture boiling freely, and a trace of hydrogen sulphide being evolved; on cooling, an oil was deposited, which, when left for a few days in a vacuum, hardened to a pale yellow, amber-like resin, still smelling of benzene. The solvent evaporates very slowly, for, on analysis eight days later, the nitrogen and sulphur, although giving the ratio  $N_2 : S$ , were both found to be more than 1 per cent. below the calculated values; eventually, the solvent was removed by gently warming the powdered substance in a flask, through which a current of dry air was kept passing for some hours; it now gave the following results:

Found  $N = 15.15$ ;  $S = 17.8$ ;  $P = 5.8$ .

$C_{24}H_{27}ON_6S_3P$  requires  $N = 15.53$ ;  $S = 17.73$ ;  $P = 5.72$  per cent.

The yield of dry solid was not far from quantitative (about 95 per cent.); no definite melting point could be observed, the substance gradually softening from  $95^\circ$  onwards, until at  $100^\circ$  it formed a liquid evolving a gas.

When shaken with cold water, the mixture gave a scarcely perceptible reaction for thiocyanic acid; if boiled, it dissolved almost entirely, evolving a little hydrogen sulphide; the solution, on cooling, deposited *p*-tolylthiocarbamide, and the mother liquor gave the reactions of thiocyanic acid, phosphoric acid and *p*-toluidine. A rough experiment, made as in the case of the corresponding phenyl homologue, gave, for 1 mol. of substance, five-sixths of a mol. of *p*-tolylthiocarbamide.

*Action of  $\alpha$ -Naphthylamine* (3 mols.).—On mixing the reagents, precisely the same phenomena were observed as in the case of aniline, the product being a doughy mass, which quickly hardened; when broken up, washed, and dried, it formed a pale yellow powder, the weight of which amounted to 96 per cent. of that of the materials used.

Found,  $S = 14.85$ ;  $P = 4.6$ .

$C_{33}H_{27}ON_6S_3P$  requires  $S = 14.77$ ;  $P = 4.77$  per cent.

Heated in a narrow tube, it frothed up at  $119$ — $120^\circ$ ; cold water had no effect on the finely-powdered substance; when heated, phosphoric and thiocyanic acids passed into solution, and a bulky, white solid was left, which was recrystallised from alcohol and identified as  $\alpha$ -naphthylthiocarbamide.

Another experiment was made, using only one molecular proportion of  $\alpha$ -naphthylamine; the semi-solid product, which amounted to 96 per cent. of the weight of materials taken, presently became hard and brittle. It had properties resembling those of the corresponding aniline derivative, but was dirty orange in colour, and gave very unsatisfactory numbers on analysis, every attempt to purify the substance having failed.

*Action of Benzylaniline.*—When equal mols. were brought together in benzene solution, the mixture became warm, but remained clear. On cooling, small, white crystals separated, which were thoroughly washed with benzene; they melted sharply at 137—138° (uncorr.) and amounted to exactly the sum of the weights of the materials employed.

Found, N = 13.9; S = 21.2; P = 7.1;

$C_{16}H_{13}ON_4S_3P$  would require N = 13.89; S = 23.78; P = 7.67 per cent.

The substance was insoluble in cold water, the mixture being neutral, and giving no red coloration with ferric chloride; on boiling, there was little sign of solution, but the iron salt now produced a distinct reddening. Warm dilute caustic potash attacked the compound, forming a basic oil, probably benzylaniline, and the solution contained much thiocyanic acid. But the mixture with caustic potash was not desulphurised by boiling with lead tartrate, and the alcoholic solution darkened only slightly when treated with ammoniacal silver nitrate, so that the product of hydrolysis did not contain any considerable proportion of *aa*-phenylbenzylthiocarbamide (Trans., 1893, 63, 325). The analytical numbers for sulphur and phosphorus being unsatisfactory, an attempt was made to crystallise the substance from alcohol, but the product, an acid syrup, refused to crystallise, and the experiment was abandoned.

#### *Summary and Conclusion.*

It appears from the foregoing experimental work that phosphoryl thiocyanate is a definite chemical compound, behaving towards water exclusively as a thiocyanate. Distilled phosphorus thiocyanate, although apparently a definite substance, can be resolved, by treatment with water, into two fractions, one of which, like the whole of the phosphoryl compound, is hydrolysed with ease, whilst the other fails to undergo hydrolysis, except to a minimal extent, although its physical properties (specific gravity and boiling point) are practically the same as at first. Moreover, between that portion which no longer reacts with water and the original distillate, which may lose about half its substance by contact with this liquid, there is no material difference as regards power to combine with aniline, for either can unite with 3 mols. of this base, but holding only a portion (approximately one-third) of this amount in ordinary thiocarbamidic combination. So far, therefore, as total aniline-fixing power is concerned, it does not appear to matter whether the phosphorous derivative holds its  $\cdot CNS$  groups in a form capable of acting towards water as  $\cdot SCN$  or otherwise: in any case, one of the three will behave as  $\cdot NCS$  towards the base.

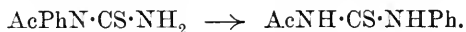
Consistently with this unexpected result, phosphoryl thiocyanate, notwithstanding that water eliminates the whole of its  $\cdot CNS$  as

thiocyanic acid (the formation of *isoperthiocyanic acid* is easily explained by the interaction of the liberated phosphoric and thiocyanic acids), can also fix three mols. of aniline, of which only one appears as phenylthiocarbamide, when the product is hydrolysed. Again, if only one molecular proportion of aniline is presented to one of phosphoryl thiocyanate, it will not distribute itself uniformly over the contained  $\cdot\text{SCN}$ , but will unite entirely with a single group, which behaves as  $\cdot\text{NCS}$  in this sense, that practically the whole of the combined base may on hydrolysis be recovered as phenylthiocarbamide. In like manner, if the phosphorous analogue, deprived by washing of practically all its power of behaving towards water as thiocyanate, is treated with one mol. of aniline, the latter will be so fixed that it may be almost completely recovered in the form of phenylthiocarbamide; but if the additive product be combined with an additional 2 mols. of aniline, the compound thus obtained will still give only one mol. of phenylthiocarbamide when hydrolysed.

The hydrolytic experiments were usually completed within a few minutes, the temperature being in the neighbourhood of  $80^\circ$ , so that the process, as conducted, could not lead to any material isomeric rearrangement of whatever basic thiocyanate might be formed; in these circumstances, the amount of substituted thiocarbamide produced was taken as a measure of the thiocarbimidic power available in each substance.

Wheeler has proposed the treatment with thiolacetic acid as a means of distinguishing between thiocyanates and thiocarbimides (*J. Amer. Chem. Soc.*, 1901, 23, 285; *Amer. Chem. J.*, 1901, 26, 348), the substances which yield carbon disulphide (and substituted amide) being regarded as thiocarbimides, and those which do not as thiocyanates. Although this appears to be a useful method of discrimination where hydrocarbon derivatives are concerned, it cannot be regarded as absolutely final in the case of acidic compounds; or, at most, it can only be used to decide how the  $\cdot\text{CNS}$  group behaves towards that particular substance at the moment of interaction, and this information does not go far enough with acidic thiocyanates, which are all more or less prone to undergo tautomeric change. Applying this method, he decides that acetyl thiocyanate is a true thiocyanate, a conclusion arrived at by Miquel from another point of view, and which is doubtless perfectly correct under certain conditions. But the totally different behaviour which it can exhibit on changing the conditions of interaction (Miquel calls it "abnormal") is most easily explained by supposing the compound to have assumed, for the time being, the thiocarbimidic configuration. It is conceivable that in the formation of acetylphenylthiocarbamide by the action of aniline, a compound,  $\text{AcS}\cdot\text{C}(\text{NH})\cdot\text{NHPh}$ , might be the first product; if, now, the acetyl group migrated to the

imino-group and the sulphur atom became doubly linked to carbon, the "abnormal" production of the disubstituted thiocarbamide could be explained. Indeed, the migration of the acetyl group in compounds already thiocarbamidic in structure is not unknown, Wheeler having adduced evidence (*Amer. Chem. J.*, 1902, 27, 274) that the change of Hugershoff's acetylphenylthiocarbamide (m. p. 139°) (*Ber.*, 1899, 32, 3649) into the isomeride melting at 171° occurs as follows :



With the data hitherto secured, it is not possible to state with certainty what is the mechanism whereby such changes are produced; but the author at present holds the view that in so far as a CNS compound unites spontaneously with aniline to yield a phenylated thiocarbamide or its immediate normal derivative it should be regarded as a thiocarbimide; from this standpoint, it becomes necessary to postulate the existence of tautomerism amongst certain "thiocyanates."

Another method of distinction proposed by Wheeler (*Amer. Chem. J.*, 1901, 26, 349) consists in reducing the alcoholic solution of the CNS compound with sodium, when thiocyanic acid is produced from a thiocyanate, but not from a thiocarbimide; this test, however, is too drastic for members of the acidic class. Thus, benzoyl thiocyanate unites directly with primary and secondary amines to form thiocarbamides; with alcohols, to form alkyl esters of thiocarbamic acid, and with phenylhydrazine to form a disubstituted thiosemicarbazide. Its behaviour towards water has already been mentioned. Even with ammonia, which often brings about double decomposition amongst the acidic thiocarbimides, it yields benzoylthiocarbamide, and consequently there can be no question as to the marked preponderance of thiocarbimidic character in this substance. Yet, as usual, a limit to the power of retaining the  $\cdot\text{NCS}$  configuration can be reached, for on treating the compound with sodium, thiocyanic acid passes into solution. Wheeler also records certain observations by T. B. Johnson, showing that when it was made to interact with ethyl sodiomalonate, sodium formanilide, sodium phenoxide or ethyl sodioacetoacetate, the  $\cdot\text{NCS}$  group was removed as sodium thiocyanate.

In the light of all the facts now available with respect to the acidic "thiocyanates" as a class, it seems tolerably safe to venture the general statement that there is no known member of this class, however pronounced its thiocarbimidic characters may be, which cannot be made to behave as a thiocyanate.

Returning now to the phosphorus compounds, it must be admitted that, since no satisfactory means of purification could be found for their derivatives, the composition of the latter has been based on the analysis of somewhat ill-defined substances; on the other hand, most

of the foregoing experiments have been repeated much oftener than appears in the paper, so that the general results may be taken as being fairly trustworthy. Probably the selection of this particular class of substances as objects of study was not a happy one, seeing that even when a single CNS group is combined with an acid radicle, it may lose its definite configuration and oscillate between  $\cdot\text{SCN}$  and  $\cdot\text{NCS}$ . When two such groups are present, one may be highly active, as  $\cdot\text{NCS}$ , whilst the other is comparatively sluggish, and easily hydrolysed out of combination, as  $\cdot\text{SCN}$ , although capable ultimately of exerting its full thiocarbimide power. Under suitable conditions, the behaviour of carbonyldithiocarbimide, referred to earlier (p. 359), may be cited as a case in point. With three such groups attached to a single mineral radicle, their limited capacity to act as  $\cdot\text{NCS}$  might perhaps almost have been anticipated. On the other hand, experiments conducted with the view of obtaining mono- and di-thiocyanates of purely inorganic acid radicles have hitherto proved unsuccessful.

In conclusion, the writer desires to express his indebtedness to Mr. R. E. Doran for assistance rendered in connection with the experimental work described above.

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## XLI.—*The Action of Sodium Hypochlorite on the Aromatic Sulphonamides.*

By HENRY STANLEY RAPER, JOHN THOMAS THOMPSON, and JULIUS BEREND COHEN.

ALTHOUGH the general nature of the chemical change \* resulting from the interaction of sodium hypochlorite and the aromatic sulphonamides resembles that described by Chattaway and Orton in the case of the aromatic acylamines (Trans., 1899, 75, 1046; 1900, 77, 134, 789; Ber., 1899, 32, 3573), yet there are certain well-marked differences in the character of the products which we venture to think are not without interest.

These authors have shown that by the action of sodium hypochlorite on the acyl-anilides and -toluidides, the halogen in the first

\* A preliminary notice of this reaction has already appeared (Proc., 1901, 17, 262). We have now supplemented these experiments by extending the reaction to a number of other sulphonamides.

instance enters the para-position with respect to the amino-group if this position is free, but otherwise becomes attached to an ortho-carbon atom. The orientating effect of the sulphonic group is different; in the first instance, the halogen seeks the ortho-position with respect to the amino-group, thus the benzenesulphonamides of aniline, *p*-toluidine, *m*-4-xylydine, and  $\beta$ -naphthylamine form ortho-compounds almost exclusively. If, however, a methyl group is present and the para-position to the amino-group is free, the conditions are modified and the halogen enters either the ortho-position to the methyl group or the para-position to the amino-group. Thus, the sulphonamide of *m*-toluidine gives a derivative of 6-chloro-*m*-toluidine. There is a considerable difference also in the readiness with which the different sulphonamides react. This is very marked in the case of those bases which are substituted in the ortho-position to the amino-group. The sulphonamides of *o*-toluidine and *m*-4-xylydine are only acted on slowly, whereas the sulphonamide of  $\alpha$ -naphthylamine, which may be regarded as an *o*-substituted compound, is quite unchanged by the hypochlorite. The following table gives a list of the compounds which have been studied:

$\text{ArNH}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_5$ $\text{ArNH}_2$	Melting point of the sulphonamide.	Position of the halogen relative to the amino-group.	Melting point of the chloro- sulphonamide.
Aniline .....	110°	<i>o</i> -	129—130°
<i>o</i> -Toluidine .....	123—124	<i>p</i> -	124—125
<i>m</i> -Toluidine .....	95	<i>p</i> -	130
		<i>op</i> -dichloro- compound	114
<i>p</i> -Toluidine .....	120	<i>o</i> -	110
<i>m</i> -4-Xylydine .....	124—125	<i>o</i> -	148—149
$\alpha$ -Naphthylamine .....	168	no action	—
$\beta$ -Naphthylamine .....	97—98	<i>o</i> -	130—131

*The Action of Sodium Hypochlorite on Benzenesulphonanilide.*

Twenty grams of benzenesulphonanilide were dissolved in 200 c.c. of a solution of sodium hypochlorite (1 c.c. = 0.03 gram Cl) in the cold and left for 12 hours; the brown solution was acidified with acetic acid and the semi-solid precipitate was filtered and washed. It was then dissolved in about twice its weight of glacial acetic acid, to which a few drops of strong sulphuric acid were added, and digested for an hour on the water-bath. The product was poured into water, from which a crystalline compound separated, and, when purified by recrystallisation from dilute acetic acid, melted at 129—130°; 18 grams of the crude product or 11 grams of purified substance were obtained.

The mother liquor contained a small quantity of a semi-solid substance which slowly became crystalline, and after recrystallisation from benzene and petroleum melted at  $116^{\circ}$ . This substance is probably benzenesulphon-*p*-chloroanilide (m. p.  $121^{\circ}$ ), but it is not readily freed from oily impurity. On analysis, the substance melting at  $129$ – $130^{\circ}$  gave the following numbers :

0.292 gave 14.15 c.c. moist nitrogen at  $15.5^{\circ}$  and 758 mm.  $N = 5.66$ .

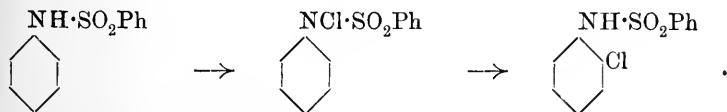
0.3185 „ 0.1764 AgCl.  $Cl = 13.57$ .

0.2097 „ 0.1820 BaSO<sub>4</sub>.  $S = 11.93$ .

C<sub>12</sub>H<sub>10</sub>O<sub>2</sub>NCIS requires  $N = 5.23$  ;  $Cl = 13.27$  ;  $S = 11.90$  per cent.

The constitution of the substance was determined by hydrolysis ; two grams were heated with about 8 c.c. of concentrated hydrochloric acid in a sealed tube at  $190^{\circ}$  for 4–5 hours. On opening the tube there was a strong odour of benzene, the presence of which was confirmed by conversion into aniline, with which sodium hypochlorite gave the usual reaction. The appearance of benzene in the decomposition of the sulphonanilide is readily accounted for, seeing that Armstrong and Field (*Ber.*, 1874, 7, 406) and Jacobsen (*Ber.*, 1876, 9, 258) have shown that sulphonic acids are converted into hydrocarbons by strong hydrochloric acid under pressure. The acid solution, after extracting with light petroleum, was made alkaline with sodium carbonate and distilled in steam ; the distillate was extracted with ether, the ether removed, and the residue dehydrated in a vacuum desiccator, when a yellow oil weighing 0.8 gram remained. The substance did not solidify on introducing a crystal of *p*-chloroaniline, even when cooled in ice ; it yielded an acetyl derivative melting at  $85$ – $86^{\circ}$  and a benzoyl derivative melting at  $102^{\circ}$ . This corresponds with *o*-chloroaniline, which was prepared for comparison and converted into the acetyl, benzoyl, and benzenesulphonyl derivatives.

The reaction probably occurs in two stages, as in the chlorination of the acetyl derivatives studied by Chattaway and Orton, although the intermediate chloroamide was too unstable to be isolated in a pure state.



The main product is therefore the *o*-chloroanilide, together with a very small quantity of the para-compound. Wallach (*Ber.*, 1877, 9, 424) found that benzenesulphonanilide, when heated at  $100^{\circ}$  with phosphorus pentachloride, yields benzenesulphon-*p*-chloroanilide (m. p.  $121^{\circ}$ ), but no reference is made to an ortho-compound. We

have repeated and confirmed Wallach's work. The product is difficult to purify, and only a small quantity of pure substance could be obtained, but we failed to detect any ortho-compound. We have also synthesised Wallach's compound from *p*-chloroaniline and benzenesulphonic chloride, and to complete the series we have also prepared benzenesulphon-*m*-chloroanilide from *m*-chloroaniline.

This anilide, which has not been previously described, melts at 121° like the para-compound.

0.2576 gave 12.85 c.c. moist nitrogen at 13° and 761 mm.;  $N = 5.76$ .

$C_{12}H_{10}O_2NClS$  requires  $N = 5.23$  per cent.

*The Action of Sodium Hypochlorite on Benzenesulphon-o-toluidide.*

Benzenesulphon-o-toluidide was described by Beckmann and Fellrath (*Annalen*, 1893, 273, 13); it crystallises from alcohol in rectangular tablets which melt at 123—124°. When treated with sodium hypochlorite in the manner already described, it gave an uncrystallisable product, but in acetic acid solution a colourless crystalline substance was obtained. If warmed with alcohol for any length of time, this compound decomposed, a portion of the alcohol being oxidised to aldehyde. From a mixture of benzene and light petroleum, the substance crystallised without any decomposition, and a product was obtained which melted at 99—100°.

0.1951 gave 0.1000 AgCl;  $Cl = 12.92$ .

$C_{13}H_{12}O_2NClS$  requires  $Cl = 12.61$  per cent.

On crystallising the foregoing compound from acetic acid solution, it becomes transformed into an isomeride melting at 124—125°.

0.1014 gave 0.0530 AgCl;  $Cl = 12.93$ .

0.1014 „ 0.0843 BaSO<sub>4</sub>;  $S = 11.41$ .

$C_{13}H_{12}O_2NClS$  requires  $Cl = 12.61$ ;  $S = 11.39$  per cent.

This substance was identified as benzenesulphon-5-chloro-*o*-toluidide, also obtained from benzenesulphonic chloride and 5-chloro-*o*-toluidine; The chlorine therefore enters the para-position to the amino-group. The isomeric substance melting at 99—100° is probably the chloro-amide,  $C_7H_7 \cdot NCl \cdot SO_2 \cdot C_6H_5$ , for on heating with alcohol it loses chlorine and reverts to the original substance. This explains both the conversion effected by acetic acid and the decomposition produced by alcohol, in which the latter reagent is oxidised to aldehyde in eliminating chlorine.

*The Action of Sodium Hypochlorite on Benzenesulphon-m-toluidide.*

Benzenesulphon-*m*-toluidide has not been previously described; it crystallises from alcohol in colourless plates melting at 95°. The action of the hypochlorite solution on this substance is much more vigorous than in the preceding cases, both mono- and di-chloro-derivatives being formed.

The *monochloro*-compound was obtained by using the theoretical quantity of sodium hypochlorite and keeping the mixture cold; after 12 hours, a large quantity of crystalline substance separated, which melted at 275—280°. This is probably a sodium derivative having the formula  $C_6H_3Cl(CH_3) \cdot NNa \cdot SO_2 \cdot C_6H_5$ ; it crystallises from ethyl acetate in fine needles.

0.8808 required 28.87 c.c. N/10  $H_2SO_4$ ; Na = 7.54.

$C_{13}H_{11}O_2NClSNa$  requires Na = 7.58 per cent.

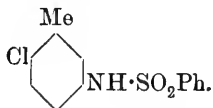
When digested for a few minutes with glacial acetic acid, the sodium compound is easily decomposed, yielding the mono-chloro-derivative, which crystallises in long, colourless prisms and melts at 130°. Five grams of the toluidide yielded 3.2 grams of the pure mono-chloro-compound.

0.3790 gave 0.1970 AgCl; Cl = 12.86.

0.3790 „ 0.3144 BaSO<sub>4</sub>; S = 11.39.

$C_{13}H_{12}O_2NClS$  requires Cl = 12.60; S = 11.37 per cent.

The constitution of the substance was determined by hydrolysis as in the previous cases. A crystalline base was obtained which melted at 83° and gave an acetyl derivative melting at 89°. These numbers correspond with the melting points of 6-chloro-*m*-toluidine and its acetyl derivative. The formula of the original compound is therefore



No other mono-chloro-compound could be detected.

*The Dichloro-compound.*—Five grams of the sulphon-*m*-toluidide were dissolved in excess of the hypochlorite solution; the whole mass subsequently solidified and was collected at the pump. After crystallisation from acetic acid, 3 grams of pure substance (m. p. 114°) and 1.7 grams of an impure product melting at about 80° were obtained. The latter is probably a mixture of the mono- and di-chloro-compounds, which are separated with difficulty. A better yield of the dichloro-compound was obtained either by warming the mixture of hypochlorite

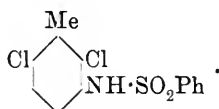
and *m*-toluidide at about 40° for a short time or by adding sodium hypochlorite solution to the monochloro-compound. The substance melting at 114° was analysed with the following result:

0.2640 gave 0.2303 AgCl. Cl = 21.60.

0.2640 „ 0.2030 BaSO<sub>4</sub>. S = 10.53.

C<sub>13</sub>H<sub>11</sub>O<sub>2</sub>NCl<sub>2</sub>S requires Cl = 22.4; S = 10.10 per cent.

On hydrolysis, a crystalline base was obtained, which was recrystallised from alcohol and melted at 58°, its acetyl derivative melting at 121°. The base was further identified by successive conversion into 2:3:6-trichlorotoluene (m. p. 45—46°), 2:3:6-trichlorobenzoic acid (m. p. 165°), and dinitro-2:3:6-trichlorotoluene (m. p. 141—142°) (compare Cohen and Dakin, Trans., 1902, 81, 1333). The structure of the sulphon dichloro-*m*-toluidide is accordingly represented as follows:



It is interesting to compare the action of the hypochlorite on the benzenesulphonyl and acetyl derivatives of *m*-toluidine. In the acetyl derivative, the hypochlorite produces substitution in the ortho- and para-positions to the methyl group (Cohen and Dakin, Trans., 1902, 81, 1332); in the sulphonamide, the chlorine atoms enter the two ortho-positions.

#### *Action of Sodium Hypochlorite on Benzenesulphon-p-toluidide.*

Benzenesulphon-*p*-toluidide was described by Wallach (*Ber.*, 1876, 9, 424), who states that it does not yield a halogen derivative with phosphorus pentachloride, and attributes the fact to the presence of the methyl group in the para-position to the amino-group. With sodium hypochlorite, the reaction goes quite smoothly, and benzenesulphon-3-chloro-*p*-toluidide (m. p. 110°) is obtained, 5 grams of the toluidide giving 3.5 grams of pure product.

0.4020 gave 0.2068 AgCl. Cl = 12.73.

0.4020 „ 0.3383 BaSO<sub>4</sub>. S = 11.54.

C<sub>13</sub>H<sub>12</sub>O<sub>2</sub>NClS requires Cl = 12.60; S = 11.37 per cent.

On hydrolysis with hydrochloric acid, 2 grams of the compound gave 0.9 gram of a yellow, oily base, which solidified on cooling in ice, and yielded an acetyl derivative melting at 118°. These properties agree with those of the 3-chloro-*p*-toluidine. The chlorine, therefore, enters the ortho-position to the amino-group. An excess of hypochlorite produced no further substitution.

*The Action of Sodium Hypochlorite on Benzenesulphon-m-4-xylylide.*

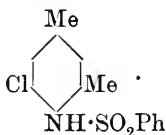
Benzenesulphon-*m*-4-xylylide, which has not been previously described, is prepared in the usual way, and crystallises in colourless prisms melting at 124—125°. When treated with sodium hypochlorite solution, it remained unchanged, but in acetic acid a small amount of chlorination product was obtained, the yield being augmented by carrying out the reaction at about 50°. The white solid which separated was recrystallised from alcohol and melted at 148—149°. Six grams of the *m*-xylylide gave 4·2 grams of pure product.

0·1293 gave 0·0619 AgCl. Cl = 11·84.

0·1293 „ 0·1004 BaSO<sub>4</sub>. S = 10·66.

C<sub>14</sub>H<sub>14</sub>O<sub>2</sub>NClS requires Cl = 11·89 ; S = 10·72 per cent.

On hydrolysis, 2 grams of the chlorination product gave 0·8 gram of a colourless, crystalline base melting at 39—40°, which formed an acetyl derivative melting at 200—201°. The base obtained on hydrolysis is identical with 5-chloro-*m*-4-xylidine.\* The sulphon-5-chloro-*m*-4-xylylide has therefore the following structure :



An excess of sodium hypochlorite had no further action.

*Sodium Hypochlorite and Benzenesulphon-α-naphthalide.*

The sulphon-α-naphthalide obtained by the action of benzenesulphonic chloride on α-naphthylamine crystallises from alcohol in colourless needles melting at 168°; it dissolves in aqueous sodium hypochlorite forming a deep brown solution, which, when poured into acetic acid, yielded a precipitate of the original substance. No change was effected by the hypochlorite in the presence of acetic acid.

*The Action of Sodium Hypochlorite on Benzenesulphon-β-naphthalide.*

Benzenesulphon-β-naphthalide crystallises from alcohol in colourless plates, which melt at 97—98°. On adding sodium hypochlorite, a yellow oil separated, which quickly solidified, the product being a

\* For purposes of identification, the preparation of the three isomeric monochloro-derivatives of *m*-4-xylidine was undertaken, and an account of these substances will appear separately.

sodium derivative of benzenesulphonchloro- $\beta$ -naphthalide, which crystallises in glistening needles from benzene containing about 5 per cent. of alcohol.

0.8837 required 2.45 c.c.  $\text{NH}_4\text{SO}_4$ .  $\text{Na} = 6.38$ .

$\text{C}_{16}\text{H}_{11}\text{O}_2\text{NClSNa}$  requires  $\text{Na} = 6.76$  per cent.

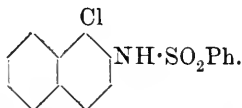
The sodium compound was decomposed by boiling for a few minutes with dilute mineral acid; the product dissolved in alcohol, from which it crystallised in colourless needles melting at  $130\text{--}131^\circ$ ; 5 grams of  $\beta$ -naphthalide gave 4 grams of pure substance.

0.1843 gave 0.0840  $\text{AgCl}$ .  $\text{Cl} = 11.28$ .

0.1843 „ 0.1355  $\text{BaSO}_4$ .  $\text{S} = 10.10$ .

$\text{C}_{16}\text{H}_{12}\text{O}_2\text{NClS}$  requires  $\text{Cl} = 11.18$ ;  $\text{S} = 10.08$  per cent.

The compound is more easily hydrolysed than the benzenesulphonotoluidides, a temperature of  $140^\circ$  for one hour being sufficient for the purpose; 1.8 grams gave 0.7 gram of solid base, which melted at  $60^\circ$  and formed an acetyl derivative melting at  $147\text{--}148^\circ$ . These data correspond with the melting points of 1-chloro- $\beta$ -naphthylamine and its acetyl derivative. The sulphonamide, therefore, has the following structure:



In this case, the chlorine atom enters the  $\alpha$ -position contiguous to the amidic nitrogen.

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## XLII.—*The Esterification of r-Mandelic Acid by Menthol and Borneol.*

By ALEXANDER McKENZIE.

It has been shown by Marckwald and Chwolle (Ber., 1898, 31, 783) that the resolution of an *i*-acid into its optically active components by means of alkaloids is due solely to the difference in solubility between the alkaloidal salts of the *d*- and *l*-acids respectively, and not, as Pasteur supposed, to any difference in affinity exhibited by the two enantiomorphous acids towards one and the same base. This conclusion was based on the following observations: (1) that corresponding

amounts of the acid cinchonine salts of *d*- and *l*-tartaric acids respectively exhibited in solution the same rise of boiling point, (2) that the rate of hydrolysis of methyl *d*-tartrate by nicotine was the same as that of methyl *l*-tartrate, and (3) that, when methylethylacetic acid in aqueous solution was shaken with a quantity of brucine insufficient for complete neutralisation, the uncombined acid was optically inactive. The formation of a salt, therefore, by union of an active acid with an active base takes place practically instantaneously, and may be considered as being essentially an ionic reaction.

Whilst, then, a *d*-acid combines with an active base with the same velocity as its *l*-isomeride, the case might conceivably be different when the action depends on the spacial arrangement of the atoms in the molecule. That ester formation is a case in point is sufficiently indicated by the experiments of Menschutkin on the dependence of the rate of ester formation on the structure of the carbon chain, and by those of V. Meyer on diortho-substituted aromatic acids. The basis of Pasteur's two crystallisation methods for resolving *i*-compounds is undoubtedly physical, but his third method, the use of micro-organisms, is probably biochemical (compare E. Fischer, *Zeit. physiol. Chem.*, 1898, 26, 60). On those considerations, Marckwald and McKenzie (*Ber.*, 1899, 32, 2120) studied the esterification of *r*-mandelic acid by *l*-menthol and isolated *l*-mandelic acid by a chemical method, distinct from Pasteur's biological method in so far that the substances concerned are of known composition.

When *r*-mandelic acid was heated with *l*-menthol at 155°, the unesterified acid was lævorotatory, and from it a specimen of *l*-mandelic acid was prepared. The rate of ester formation of the enantiomorphous acids towards one and the same active alcohol was accordingly different, since *l*-menthyl *d*-mandelate was formed more quickly than *l*-menthyl *l*-mandelate. The esterified product, on the other hand, which was expected to contain an excess of *l*-menthyl *d*-mandelate, did not, however, yield a dextrorotatory acid on hydrolysis, but was either inactive or feebly lævorotatory. It appeared, in fact, as if the *r*-acid was being converted into the *l*-isomeride without a corresponding production of the *d*-isomeride. In order to account for this confusing result, experimental evidence was subsequently (*Ber.*, 1901, 34, 469) submitted to show that *l*-menthyl *d*-mandelate suffers partial racemisation during its formation more quickly than *l*-menthyl *l*-mandelate. Similar results were obtained (*loc. cit.*) with *i*-phenylethoxyacetic acid, but with *i*-ethoxypropionic acid there was no abnormality, since the rotation of the acid recovered from the esterified product was of the opposite sign to that of the unesterified acid.

Now Victor Meyer has found that in the case of two isomeric aromatic esters, the particular one which is formed with the greater

difficulty is also the less readily hydrolysable. His conclusion is based on experiments made with chloronaphthoic, bromobenzoic, and other acids (*Ber.*, 1895, 28, 1262), and has been confirmed by Wegscheider (*Ber.*, 1895, 28, 1468) and by Brühl (*Ber.*, 1895, 28, 1913, 2868). Accordingly, *l*-menthyl *d*-mandelate and *l*-menthyl *l*-mandelate, which are not mirror-images, undergo hydrolysis by the same inactive base at different rates. Of the two, the former is the more quickly produced and is the more quickly hydrolysable. The mixture of unequal amounts of the two esters, which, on complete hydrolysis, yielded a feebly lævorotatory acid, gave, on partial hydrolysis, a dextrorotatory acid.

The applicability of this method for resolving inactive compounds was further exemplified (*Ber.*, 1901, 34, 469) in [the case of *sec*-octyl alcohol. Whilst the difference in the rate of formation of the tartrates of *d*- and *l*-octyl alcohols was slight, there was a marked difference in their rate of hydrolysis, so that, by the method of fractional hydrolysis, a partial resolution of the *i*-alcohol was effected. In this connection, attention has already been directed (*Ber.*, 1900, 33, 210) to the fact that Frankland and Price, in the esterification of racemised amyl alcohol by *d*-glyceric acid, observed that the unesterified alcohol was feebly lævorotatory (*Trans.*, 1897, 71, 253).

In the light of the results obtained by Marckwald and the author, Walden has interpreted observations made by him during the investigation, firstly, of the action of active amyl alcohol on inactive  $\alpha$ -bromopropionic bromide, and, secondly, of the action of active amyl iodide on inactive silver methylsuccinate (*Ber.*, 1899, 32, 2703). Scholtz has studied the action of active amyl iodide on inactive 1-methyl-2-pipecoline in the hope that the formation of the quaternary iodide of the *d*-base would take place with a velocity different from that of the formation of the iodide of the *l*-base (*Ber.*, 1901, 34, 3015); he obtained, however, only negative results.

The following experiments include an examination of the action of borneol on *r*-mandelic acid, whilst the interaction of *l*-menthol and *r*-mandelic acid has also been further investigated.

## EXPERIMENTAL.

### *Esterification of r-Mandelic Acid by Borneol.*

*Expt.* 1.—The borneol employed had the rotation  $[\alpha]_D^{18} - 37.4^\circ$  ( $c = 17.374$ ) in ethyl-alcoholic solution, a value in agreement with that of Haller (*Ann. Chim. Phys.*, 1892, [vi], 27, 395). Twenty grams of *r*-mandelic acid were heated with 20 grams of *l*-borneol in an oil-bath at  $150^\circ$  for  $1\frac{1}{4}$  hours. The product was dissolved in ether and the

unesterified acid separated from the esters by shaking the ethereal solution with a dilute aqueous solution of sodium carbonate. In order to separate effectively any traces of borneol or borneol esters present in the solution of sodium mandelate, the latter was concentrated by evaporation on the water-bath and then extracted with ether. It was next acidified and extracted with ether, when 9.3 grams of mandelic acid were obtained with the following specific rotation in aqueous solution:  $l=2$ ;  $c=7.48$ ;  $\alpha_D^{20^\circ} - 0.58^\circ$ ;  $[\alpha]_D^{20^\circ} - 3.9^\circ$ .

After distilling the ether from the ethereal solution containing the esters, the latter were hydrolysed by heating with an excess of alcoholic potassium hydroxide. When the alcohol had been removed, water was added and the precipitated borneol drained off. The filtrate was completely freed from borneol as before; the mandelic acid isolated from it by acidification and extraction with ether was slightly lævorotatory, the following data being obtained in aqueous solution:  $l=2$ ;  $c=8.54$ ;  $\alpha_D^{20^\circ} - 0.25^\circ$ ;  $[\alpha]_D^{20^\circ} - 1.5^\circ$ .

This experiment shows that *d*-mandelic acid is esterified by *l*-borneol more quickly than is *l*-mandelic acid. The unesterified acid is lævorotatory, but the mixture of esters formed did not yield a dextro-rotatory acid, but a feebly lævorotatory one. The latter result is to be attributed to the unequal rates of racemisation of *l*-bornyl *d*-mandelate and *l*-bornyl *l*-mandelate, the former being racemised during its formation more quickly than the latter.

*Expt. 2.*—In order that the esterification might be more complete than in the previous case, 20 grams of *r*-mandelic acid were heated with 20 grams of *l*-borneol for 6 hours at  $150^\circ$ . The product was manipulated as before; 3.7 grams of unesterified acid were recovered, and a determination of its specific rotation gave the following result:  $l=2$ ;  $c=7.4$ ;  $\alpha_D^{14^\circ} - 1.07^\circ$ ;  $[\alpha]_D^{14^\circ} - 7.2^\circ$  (in aqueous solution).

The acid (15.5 grams) obtained by hydrolysing the mixed esters by an excess of alcoholic potassium hydroxide was feebly lævorotatory, thus,  $l=2$ ;  $c=10$ ;  $\alpha_D^{14^\circ} - 0.27^\circ$ ;  $[\alpha]_D^{14^\circ} - 1.3^\circ$  (in aqueous solution).

*Expt. 3.*—The effect of esterifying for a longer time at a lower temperature was next examined. Ten grams of *r*-acid were heated with 30 grams of *l*-borneol for 28 hours in a water-bath heated to boiling. The unesterified acid (2.6 grams) had the following rotation:  $l=2$ ;  $c=10.4$ ;  $\alpha_D^{13^\circ} - 2.18^\circ$ ;  $[\alpha]_D^{13^\circ} - 10.5^\circ$  (in aqueous solution).

The acid (6.6 grams) obtained from the esters was again feebly lævorotatory,  $l=4$ ;  $c=10.4$ ;  $\alpha_D^{18^\circ} - 0.17^\circ$ . This sign of rotation was confirmed by crystallising the 6.6 grams from water, withdrawing a crop of the *r*-acid and finding that the filtrate was lævorotatory.

The 3.7 grams of acid from *Expt. 2* and the 2.6 grams from *Expt. 3* were united and crystallised from water. After the removal of 3.1 grams of *r*-acid, the filtrate was converted into magnesium

salt; a small crop of magnesium *r*-salt was withdrawn, and the filtrate from this acidified and extracted with ether. The resulting acid was next converted into cadmium salt, from the aqueous solution of which a crop of cadmium *r*-mandelate was withdrawn, and the filtrate then decomposed by hydrogen sulphide. The resulting acid gave the following result:  $l=2$ ;  $c=1.586$ ;  $\alpha_D^{18} - 3.53^\circ$ ;  $[\alpha]_D^{18} - 111.3^\circ$  (in aqueous solution). The isolation of the pure *l*-acid was not, however, attempted in this case, the object of the experiment being simply to show how the *r*-acid may be gradually eliminated from a mixture containing a large excess of it, together with a little of the *l*-isomeride.

*Expt. 4.*—When *r*-mandelic acid (1 mol.) was heated with Kahlbaum's dextrorotatory borneol (1 mol.) for 1 hour at  $155^\circ$ , the unesterified acid was dextrorotatory,  $l=4$ ;  $c=10$ ;  $\alpha_D^{20} + 1.80^\circ$ ;  $[\alpha]_D^{20} + 4.5^\circ$ ; whilst the esterified product yielded a slightly dextrorotatory acid.

The rotation of the borneol used,  $[\alpha]_D^{18} + 23^\circ$  for  $c=18.144$  in ethyl alcoholic solution, indicated that it was a mixture of *d*- and *iso*-borneols.

*Expt. 5.*—*r*-Mandelic acid was next so completely esterified by *l*-borneol in such a manner that no fractional esterification took place. The *l*-bornyl *d**l*-mandelate was then submitted to fractional hydrolysis. Ten grams of *r*-acid were heated in a boiling water-bath for seven hours with 30 grams of *l*-borneol, a current of dry hydrogen chloride being passed into the mixture from time to time. The product was dissolved in ether and shaken with dilute aqueous sodium carbonate until all the free acid had been removed. The esterification was practically complete, since only 0.2 gram of mandelic acid was recovered. After expulsion of the ether from the ethereal solution, the resulting oil was dissolved in ethyl alcohol and heated on a boiling water-bath for 10 hours with 1 gram of potassium hydroxide, an amount insufficient for the complete hydrolysis of the esters. The potassium salt, when freed completely from the residual borneol and unesterified oil, yielded 1.7 grams of a laevorotatory acid:  $l=2$ ;  $c=6.8$ ;  $\alpha_D^{13} - 0.90^\circ$ ;  $[\alpha]_D^{13} - 6.6^\circ$  (in aqueous solution).

The residual esters, on the other hand, after being heated with a large excess of alcoholic potassium hydroxide, gave 6.8 grams of an acid, a saturated aqueous solution of which, when examined with a polarimeter, reading to  $0.01^\circ$ , was inactive, as also was the filtrate obtained after removing a crop of 5 grams.

A similar result was obtained in a subsequent experiment, where a larger amount of alkali was used in the initial hydrolysis. The mixed esters from 10 grams of acid were hydrolysed by 3.1 grams of potassium hydroxide, when 5.5 grams of acid were obtained, giving

the following data:  $l = 2$ ;  $c = 14$ ;  $\alpha_D^{20} - 1.08^\circ$ ;  $[\alpha]_D^{20} - 3.9^\circ$  (in aqueous solution).

The second hydrolysis, with excess of alkali, again gave an inactive product.

The fractional hydrolysis of *l*-bornyl *dl*-mandelate thus proceeded in an unexpected manner. Although *l*-bornyl *d*-mandelate is more readily formed than *l*-bornyl *l*-mandelate, the latter appeared to be the more readily hydrolysable of the two. The formation of *r*-mandelic acid as the product of the final hydrolysis is discussed in the sequel.

#### *Esterification of r-Mandelic Acid by l-Menthol.*

Marckwald and the author (*loc. cit.*) had previously isolated *l*-mandelic acid by means of the fractional esterification of the *r*-acid. In the following experiment, the isolation of the *d*-acid was effected by the method of fractional hydrolysis. The esterification of *r*-mandelic acid with *l*-menthol according to the Fischer-Speier method was practically complete. After removal of the mineral acid and a trace of mandelic acid, the product was hydrolysed by a calculated amount of alcoholic potassium hydroxide solution sufficient for the hydrolysis of about half of the ester mixture. The resulting solution of potassium salt was separated from the residual esters and menthol and then yielded a mixture of mandelic acids, with  $[\alpha]_D^{17} + 4.5^\circ$  ( $c = 10.075$ ) in aqueous solution. From the latter product, a specimen of *d*-mandelic acid, with the correct melting point and specific rotation, was isolated by the method of separation for the *l*-acid indicated by Marckwald and the author.

The difference in the rate of hydrolysis of the two esters under consideration is more marked towards the beginning of the hydrolysis than later, since a more active product than in the case just described may be obtained by lessening the amount of alkali in the initial hydrolysis. Thus, when 10 grams of *r*-acid were heated with 30 grams of menthol in the presence of hydrochloric acid, and the product, after the removal of the free acid, was partially hydrolysed by an amount of alkali considerably less than half that required for complete hydrolysis, 1.2 grams of acid were obtained having  $[\alpha]_D^{10} + 11.3^\circ$  ( $c = 4.8$ ) in aqueous solution. The residual esters yielded 6.5 grams of an acid with  $[\alpha]_D - 2.5^\circ$  ( $c = 13$ ) in aqueous solution. It should be noted, however, that the latter hydrolysis was quickly conducted by heating on the water-bath for half an hour with an amount of alcoholic potassium hydroxide just sufficient for the purpose.

*l*-Menthyl *dl*-mandelate was prepared by heating *r*-mandelic acid on a boiling water-bath for 10 hours with 3 times its weight of *l*-menthol in presence of hydrogen chloride. From the ethereal solution of the

product, the free acid was removed by dilute sodium carbonate, when it was found that only a trace of mandelic acid was obtained, from which it was concluded that the esterification was practically complete. After the ethereal solution had been dried, the ether was expelled and the oil distilled under diminished pressure. The menthol was completely removed and finally an oil, boiling at  $225^{\circ}$  under 30 mm. pressure, distilled over; this quickly solidified to a hard cake, which on analysis gave  $C=74.4$ ;  $H=9.0$ ;  $C_{18}H_{26}O_3$  requires  $C=74.5$ ;  $H=9.0$  per cent.

The product, which dissolves only sparingly in light petroleum, from which it separates in feathery, asbestos-like crystals, is readily soluble in benzene, chloroform, ethyl acetate, acetone, or pyridine, and moderately so in ethyl alcohol, from which it crystallises in needles. It is practically insoluble in water, with which it may be boiled for several hours without undergoing any appreciable hydrolysis. It melts at  $85-86^{\circ}$ . A determination of its rotation in ethyl alcoholic solution gave the following result:  $l=2$ ;  $c=10.890$ ;  $\alpha_D^{18} - 16.17^{\circ}$ ;  $[\alpha]_D^{18} - 74.2^{\circ}$ .

Frankland first suggested the possibility of the resolution of esters of this type by submitting them to fractional crystallisation (*Pasteur Memorial Lecture*, Trans., 1897, 71, 696. Compare also Wohl, *Ber.*, 1898, 31, 2394), and Frankland and Price have shown (Trans., 1897, 71, 253) that, although the ester formed from active amyl alcohol and *i*-dibenzoylglyceric acid is distinctly crystalline, no separation took place on crystallisation. A similar experience to the latter was encountered when the mandelate just described was crystallised from light petroleum and when the individual crops were allowed to separate at the temperature of the laboratory. The crystalline form of successive crops appeared to be perfectly homogeneous. After 10 crystallisations, the melting point of the product was the same as that of the original substance, whilst  $[\alpha]_D^{21}$  in ethyl alcoholic solution was  $-72.7^{\circ}$  ( $c=4.5624$ ), a value agreeing with that previously quoted; the result was the same when the ester was repeatedly crystallised from ethyl alcohol, no resolution having been effected.

*l*-Menthyl *dl*-mandelate is accordingly a partially racemic compound, and further attempts are being made to resolve it by varying the temperature conditions.

When *l*-menthyl *dl*-mandelate is hydrolysed with an excess of alcoholic potassium hydroxide, it yields *r*-mandelic acid. When hydrolysed with an amount of alkali insufficient for complete hydrolysis, but in considerable excess of that necessary for the hydrolysis of half the ester, the resulting potassium salt yields a *l*-vortatory acid: 14.5 grams of the ester (corresponding with 7.6 grams of acid) were hydrolysed in the manner indicated and, from

the potassium salt, 6 grams of acid were recovered giving the following data:  $l = 4$ ;  $c = 12$ ;  $\alpha_D - 2.08^\circ$ ;  $[\alpha]_D - 4.3^\circ$  in aqueous solution.

The residual esters, when hydrolysed with an excess of alkali, yielded 1.1 grams of inactive acid.

It is therefore possible by the fractional hydrolysis of *l*-menthyl *d**l*-mandelate to obtain either a dextrorotatory or levorotatory acid from the initial hydrolysis, according to the amount of alkali used. When the amount of alkali used is much less than that required for the hydrolysis of half the mixed esters, the acid resulting from the potassium salt formed is dextrorotatory. When the concentration of the alkali is increased, a larger quantity of dextrorotatory acid is obtained, the specific rotation of which is smaller than in the former case. Finally, by increasing still further the concentration of the alkali, a levorotatory acid is obtained.

In the experiments on fractional hydrolysis described in this paper, it has been repeatedly observed that the final hydrolysis of the mixed esters with alcoholic potassium hydroxide in excess led to the formation of a totally racemised product, and the following experiments were accordingly conducted. Five grams of *l*-mandelic acid, melting at  $133^\circ$  and having  $[\alpha]_D - 158^\circ$  in aqueous solution, were esterified by heating on a boiling water-bath for 7 hours with 15 grams of *l*-menthol in presence of hydrogen chloride. Alcoholic potassium hydroxide was then added to the product and the mixture boiled for 2 hours. After removal of the alcohols, the acid, recovered from the potassium salt, melted at  $116-118^\circ$  and gave  $[\alpha]_D - 3.3^\circ$  ( $c = 7.7436$ ) in aqueous solution.

In an experiment conducted with *l*-borneol in an analogous manner, the recovered acid gave  $[\alpha]_D - 9.7^\circ$  ( $c = 6.432$ ) in aqueous solution.

Although it has been shown that *l*-mandelic acid yields *i*-phenylchloroacetic acid when heated with fuming hydrochloric acid at  $95-100^\circ$  in a sealed tube (Easterfield, Trans., 1891, 59, 72), and that *d*-mandelic acid by the action of phosphorus pentachloride sometimes yields *i*-phenylchloroacetyl chloride (Kipping, Trans., 1903, 83, 1005), it was not considered probable that the partial racemisation observed in the experiments quoted took place during the actual esterification of the acid, but rather during the subsequent hydrolysis. That excess of alkali does actually racemise potassium *l*-mandelate was shown by experiment.

One gram of *l*-mandelic acid was added to a solution of 4 grams of potassium hydroxide in 30 c.c. of water. The solution, examined in a 2-dm. tube, gave about  $\alpha_D^{15^\circ} - 7.6^\circ$ , and did not appear to racemise after 12 hours at the temperature of the laboratory. After being heated for several hours on the water-bath, the solution was quite inactive and yielded *r*-mandelic acid melting at  $119^\circ$ .

Similarly, when *l*-mandelic acid was heated with a considerable excess of alcoholic potassium hydroxide, the solution became quite inactive and yielded *r*-mandelic acid.

The action of alkali on optically active esters and on the salts of optically active acids is being further examined.

*Summary.*

(1) When *r*-mandelic acid was heated with *l*-borneol, the unesterified acid was lævorotatory. The mixture of esters yielded a lævorotatory acid.

(2) When *l*-bornyl *dl*-mandelate was submitted to fractional hydrolysis, a lævorotatory acid was obtained from the initial hydrolysis, and an inactive acid from the final hydrolysis.

(3) *d*-Mandelic acid was isolated from the dextrorotatory acid obtained from the initial hydrolysis of *l*-menthyl *dl*-mandelate.

(4) *l*-Menthyl *dl*-mandelate yields either a dextrorotatory or a lævorotatory acid from the initial fractional hydrolysis, according to the amount of alkali used.

(5) *l*-Menthyl *dl*-mandelate is a partially racemic compound, which is not resolved into *l*-menthyl *d*-mandelate and *l*-menthyl *l*-mandelate when repeatedly crystallised from light petroleum at the temperature of the laboratory.

(6) Potassium *l*-mandelate undergoes complete racemisation when heated with a large excess of potassium hydroxide in aqueous or in alcoholic solution.

The author desires to express his thanks to the Research Fund Committee of the Chemical Society for a grant, which defrayed the cost of this research.

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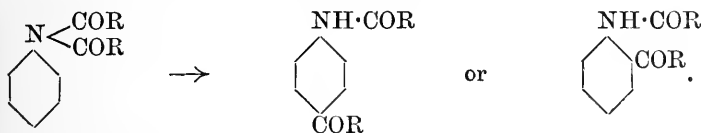
### XLIII.—*Isomeric Change of Diacylanilides into Acyl-aminoketones.*

By FREDERICK DANIEL CHATTAWAY.

A LARGE number of derivatives of aromatic amines in which aminic hydrogen is replaced by various atoms or groups readily undergo an intramolecular rearrangement, the substituting atom or group changing place with a hydrogen atom of the nucleus. Such exchange invariably occurs between the substituting atom or group and a

hydrogen attached to the nucleus in an ortho- or a para-position with respect to the amino-group, interchange between a group attached to the nitrogen and a hydrogen atom in either meta-position never having been observed. The transformations which have been most thoroughly studied are those in which alkyl, nitroxyl, or halogen radicles are concerned; the ready substitution of aromatic amines by agents such as nitric acid, chlorine, or bromine is due to changes of this type which are brought about with great ease.

Although the acyl groups very readily replace aminic hydrogen, these radicles have up to the present not been observed to migrate into the nucleus, although the diacylanilides are well known. Such intramolecular changes, however, can be effected readily, and the reactions, in so far as they have been studied, follow a course exactly similar to that of other analogous transformations, thus:



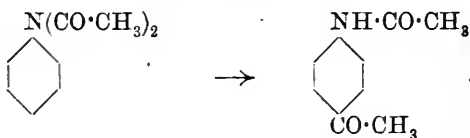
These intramolecular rearrangements take place at somewhat high temperatures and under the influence of catalytic agents, hydrogen chloride being always effective, whilst in some cases zinc chloride gives a better yield. Transference of more than one acyl group into the nucleus has, however, not yet been effected.

Owing to the reactive character of the resulting ketones, the yields are never quantitative, and resinous or tarry by-products are always produced. When acetylation or benzylation of an aromatic amine is effected by heating the base with the acid chloride, the product is invariably coloured and small quantities of tarry matters may be formed. This is without doubt due to the occurrence, to a slight extent, of the isomeric change under consideration, and to the formation of resinous products from the resulting ketone.

The transformation of dibenzanilide into benzoylaminobenzophenone is the only one in which both the ortho- and the para-isomerides have been isolated in quantity, and it is this case which brings these changes into complete accord with other analogous intramolecular rearrangements. This transformation is the only simple method by which *o*-aminobenzophenone has yet been obtained.

The change of diacetanilide into acetylaminacetophenone and of dipropionanilide into propionylaminopropiophenone where only the para-derivatives have been satisfactorily isolated have also been studied.

*Transformation of Diacetanilide into Acetyl-p-aminoacetophenone,*



Acetanilide, when heated with an equivalent quantity of acetic anhydride or acetyl chloride for some time, yields diacetanilide, which can be obtained pure by distillation.

If diacetanilide is mixed with about 10 per cent. of dry powdered zinc chloride and heated at 150—160° for several hours, or if at this temperature, it is treated with a slow current of dry hydrogen chloride, transformation takes place, and a considerable amount of the isomeric acetyl-*p*-aminoacetophenone is produced. There are clear indications of the simultaneous formation of the isomeric acetyl-*o*-aminoacetophenone, but the compound cannot be isolated with certainty, very probably because during the heating it becomes hydrolysed to some extent, and then, under the influence of the zinc chloride, reacts with the *p*-aminoacetophenone simultaneously formed to produce  $\alpha$ -*p*-aminophenyl- $\gamma$ -lepidine. This substance is always found as a product of the reaction and, as O. Fischer has shown (*Ber.*, 1886, 19, 1038), it is formed almost quantitatively when a mixture of *o*- and *p*-aminoacetophenones is heated together with zinc chloride. Some difficulty is experienced in isolating the different products, as much tarry or resinous matter is produced which is probably formed either by some complicated condensation of the aminoketones or from the unstable aminophenylacetylenes derived from these compounds by the action of the condensing agent (compare Baeyer, *Ber.*, 1882, 15, 2174).

The following process is found to give the best results: diacetanilide is heated at about 140—150° for 8—10 hours and a very slow current of hydrogen chloride is passed through the melted mass; a viscid, brown liquid is produced which solidifies on cooling, and from which acetyl-*p*-aminoacetophenone can be obtained by long-continued crystallisation, but as the process is very tedious the base is best extracted in the following manner. The product is completely dissolved in excess of alcohol containing about one-third of its bulk of concentrated hydrochloric acid and hydrolysed by boiling for 6—8 hours; the resulting liquid is made slightly alkaline with caustic soda and distilled in a current of steam, which removes the aniline obtained from the untransformed diacetanilide, about 50 per cent. of the aniline used being thus recovered. The alkaline liquid in the distilling

flask is cooled and the tarry residue collected, the *p*-aminoacetophenone being obtained from this by repeated extractions with boiling water. These solutions can be decolourised by heating with animal charcoal and concentrated, if necessary, when the para-base, which separates on cooling, can be extracted with ether.

If the steam distillation is continued for some time after the aniline has passed over, a pale yellow distillate is obtained having an intensely penetrating odour and reddening a pine splinter previously moistened with hydrochloric acid. This distillate undoubtedly contains a little of the ortho-base, and a yellow oil can be extracted from it by ether, but the amount produced is so extremely small that it cannot be identified with certainty. The yield of *p*-aminoacetophenone is not good and seldom exceeds 5 per cent. of the weight of diacetanilide used.

With zinc chloride as catalyst, the yield is better, being generally about 25 per cent. Diacetanilide is intimately mixed with about an eighth of its weight of zinc chloride and heated at 150° for 12 hours. The product is poured into boiling water, washed several times to remove the zinc chloride, and then treated in the foregoing manner.

This method is similar to that employed by Klingel (*Ber.*, 1885, 18, 2687) in preparing *p*-aminoacetophenone, except that diacetanilide is used in place of acetanilide and acetic anhydride in order to demonstrate the transformation. Klingel regarded the action as consisting of a direct introduction of the acetyl group into the ring without the formation of any intermediate product. There can, however, be no doubt that diacetanilide is formed in his method, the *p*-aminoacetophenone being produced by the transformation of the diacetyl compound.

A number of derivatives of *p*-aminoacetophenone have been prepared; these are formed by the ordinary processes, but in the preparation of the nitrogen-halogen derivatives great care must be taken to avoid the liberation of free halogen. The chloroamino-derivatives are prepared by suspending or dissolving the acylamino-ketone in chloroform and shaking it for some time with a well-cooled solution of potassium hypochlorite containing an excess of potassium hydrogen carbonate. On separating the chloroform solution, drying with calcium chloride, and evaporating off the solvent in a current of dry air, a yellow, viscid liquid is left, which, if pure, at once solidifies to a colourless, crystalline mass, on cooling and stirring with a little light petroleum.

The bromoamino-derivatives are made and treated in a similar way, using a solution of hypobromous acid to which a little freshly precipitated mercuric oxide has been added to prevent any liberation of free bromine.

The compounds, unless otherwise stated, were crystallised from a mixture of chloroform and petroleum (b. p. 60—80°).

*Acetyl-p-chloroaminoacetophenone*,  $\text{CH}_3 \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{NCl} \cdot \text{CO} \cdot \text{CH}_3$ , crystallises in clusters of glistening, pearly plates and melts at 92°.

0.2056 liberated I from 19.5 c.c. *N*/10 solution. Cl (as NCl) = 16.81.

$\text{C}_{10}\text{H}_{10}\text{O}_2\text{NCl}$  requires Cl (as NCl) = 16.75 per cent.

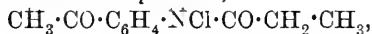
*Acetyl-p-bromoaminoacetophenone*,  $\text{CH}_3 \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{NBr} \cdot \text{CO} \cdot \text{CH}_3$ , crystallises from petroleum (b. p. 60—80°) in yellow, glistening, rhombic plates which melt at 83°.

0.2298 liberated I from 17.9 c.c. *N*/10 solution. Br (as NBr) = 31.14.

$\text{C}_{10}\text{H}_{10}\text{O}_2\text{NBr}$  requires Br (as NBr) = 31.22 per cent.

*Propionyl-p-aminoacetophenone*,  $\text{CH}_3 \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CH}_3$ , crystallises from alcohol in glistening, transparent, colourless prisms and melts at 136°; its composition was established by estimating the chlorine in the corresponding chloroamino-derivative.

*Propionyl-p-chloroaminoacetophenone*,



forms colourless, transparent plates which melt at 42°.

0.3020 liberated I from 26.6 c.c. *N*/10 solution. Cl (as NCl) = 15.61.

$\text{C}_{11}\text{H}_{12}\text{O}_2\text{NCl}$  requires Cl (as NCl) = 15.71 per cent.

*Benzoyl-p-aminoacetophenone*,  $\text{CH}_3 \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{C}_6\text{H}_5$ , crystallises from alcohol or chloroform in colourless, pearly plates melting at 205°.

*Benzoyl-p-chloroaminoacetophenone*,  $\text{CH}_3 \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{NCl} \cdot \text{CO} \cdot \text{C}_6\text{H}_5$ .

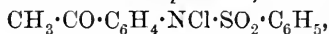
Benzoyl-p-aminoacetophenone is so sparingly soluble in cold chloroform that it is better to add its alcoholic solution to potassium hypochlorite solution containing excess of hydrogen carbonate, the mixture being then shaken with a little chloroform until all the solid has disappeared. To remove the alcohol and to ensure the conversion of all the benzoyl derivative, the chloroform solution is repeatedly shaken with fresh hypochlorous acid. *Benzoyl-p-chloroaminoacetophenone* crystallises in clusters of colourless plates which melt at 77°.

0.2511 liberated I from 18.1 c.c. *N*/10 solution. Cl (as NCl) = 12.77.

$\text{C}_{15}\text{H}_{12}\text{O}_2\text{NCl}$  requires Cl (as NCl) = 12.96 per cent.

*Benzenesulphon-p-aminoacetophenone*,  $\text{CH}_3 \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{SO}_2 \cdot \text{C}_6\text{H}_5$ , crystallises from alcohol in clusters of slender, colourless needles melting at 128°.

*Benzenesulphon-p-chloroaminoacetophenone*,



forms small, colourless, transparent plates, which are apparently flattened rhombs melting at  $91^{\circ}$ .

0.1804 liberated I from 11.6 c.c. *N*/10 solution. Cl (as NCl) = 11.39.

$C_{14}H_{12}O_3NClS$  requires Cl (as NCl) = 11.45 per cent.

*Toluene-p-sulphon-p-aminoacetophenone*,



crystallises from alcohol in colourless, transparent, flattened prisms which melt at  $203^{\circ}$ .

*Toluene-p-sulphon-p-chloroaminoacetophenone*,



forms clusters of irregular, colourless plates melting at  $93^{\circ}$ .

0.2909 liberated I from 18.1 c.c. *N*/10 solution. Cl (as NCl) = 11.03.

$C_{15}H_{14}O_3NClS$  requires Cl (as NCl) = 10.95 per cent.

*Transformation of Dipropionanilide into Propionyl-p-aminopropiophenone*,



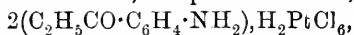
Under comparable conditions, dipropionanilide is transformed into the corresponding aminoketone exactly like diacetanilide, but only propionyl-*p*-aminopropiophenone could be isolated from the product in any quantity, although in this case also the ortho-compound is probably formed in small amount. When hydrogen chloride is used as a catalyst, the yield is small, but it is much increased by the employment of zinc chloride. The yield is better when the propionic acid formed is not separated from the dipropionanilide, about 50 per cent. of the theoretical amount being obtained in the following manner.

Propionanilide (1 mol.) is heated at  $140$ — $150^{\circ}$  for some hours with the equivalent amount (1 mol.) of propionic anhydride, then about a third of its weight of dry powdered zinc chloride is added and the heating continued for about twelve hours. The pale brown liquid produced, which solidifies on cooling, is washed with warm water to remove zinc chloride and hydrolysed by boiling for 8 hours with an excess of alcohol containing about one-sixth of its bulk of concentrated hydrochloric acid. After distilling off the alcohol in a current of steam, the residue is made slightly alkaline with caustic soda and again distilled in steam to remove any anilide obtained from unchanged dipropionanilide. On filtering the hot alkaline liquid from a very little tarry matter, the base separates from it on cooling in pale reddish-brown plates. A further

quantity can be extracted from the mother liquor by ether together with a very small amount of a pungent, oily substance which is probably the ortho-isomeride.

*p*-Aminopropiophenone as it first separates from the alkaline liquid has a somewhat reddish-brown colour, which is, however, due to slight impurity and can be completely removed by recrystallisation. The substance is moderately soluble in alcohol or chloroform, and sparingly so in ether; it crystallises from alcohol or a mixture of alcohol and ether in thick, colourless, transparent plates which are highly refractive, and separates from chloroform in colourless, transparent, four-sided, flattened rhombs melting at  $142^{\circ}$ . It readily dissolves in hydrochloric acid forming a very soluble hydrochloride which crystallises in colourless, flattened prisms.

On mixing alcoholic solutions of *p*-aminopropiophenone hydrochloride and platinic chloride, the platinichloride,

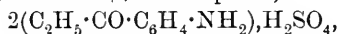


crystallises out in small, flattened, bright orange-coloured prisms with domed ends. The double salt is sparingly soluble in hot water and in alcohol and blackens just above  $200^{\circ}$ , but does not melt.

0.3813 yielded 0.1037 Pt.  $\text{Pt} = 27.19$ .

$\text{C}_{18}\text{H}_{24}\text{O}_2\text{N}_2\text{Cl}_6\text{Pt}$  requires  $\text{Pt} = 27.52$  per cent.

*p*-Aminopropiophenone easily dissolves in a hot dilute solution of sulphuric acid, and, on cooling, the sulphate,



crystallises out in glistening, colourless, pearly plates which are transparent when thin. On heating rapidly, it melts with decomposition at about  $223^{\circ}$ , turning a bright red colour; if heated slowly, it melts a few degrees lower with similar decomposition.

0.4716 yielded 0.2771  $\text{BaSO}_4$ .  $\text{SO}_4 = 24.18$ .

$\text{C}_{18}\text{H}_{24}\text{O}_6\text{N}_2\text{S}$  requires  $\text{SO}_4 = 24.24$  per cent.

Acetyl-*p*-aminopropiophenone,  $\text{C}_2\text{H}_5\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_3$ , is easily prepared by adding the calculated quantity of acetic anhydride to the base, when considerable heat is developed and a crystalline mass separates. On completing the action by warming for a short time on the water-bath, freeing from acid by a dilute solution of potassium hydrogen carbonate, and repeatedly crystallising from alcohol, the compound is obtained in perfectly colourless, long, glistening, six-sided prisms terminated by pyramids which melt at  $175^{\circ}$ .

Kunckell (*Ber.*, 1900, 33, 2641), who first prepared acetyl-*p*-aminopropiophenone by the action of propionyl chloride on acetanilide in the presence of a large excess of aluminium chloride, states that it forms pale yellow needles melting at  $161^{\circ}$ , and that the *p*-aminopropio-

phenone obtained from this formed long, yellow needles melting at  $140^{\circ}$ . The colour noted in both cases is without doubt due to a slight impurity. In this method of preparation also, it is probable that the aminoketone is formed by the transformation of propionylacetanilide under the influence of the aluminium chloride, and the very low melting point given by Kunckell for the acetyl derivative ( $14^{\circ}$  below that obtained by the author) seems to support this view, as in the transformation of the mixed anilide it is almost certain that the acetyl group as well as the propionyl group would be transferred to the ring, and that the product, however carefully purified, would retain a small quantity of admixed propionyl-*p*-aminoacetophenone.

From the base obtained in the above transformation, a number of derivatives have been made.

The nitrogen chloride and bromide derivatives of the acylamino-propionophenones were all prepared by adding an alcoholic solution of the acylaminoketone to a cooled solution of potassium hypochlorite containing hydrogen carbonate or to a solution of hypobromous acid containing suspended mercuric oxide. In the case of the benzoyl derivatives, a large quantity of warm alcohol was required.

*Acetyl-p-chloroaminopropionophenone*,  $C_2H_5 \cdot CO \cdot C_6H_4 \cdot NCl \cdot CO \cdot CH_3$ , crystallises in colourless plates melting at  $75^{\circ}$ .

0.2262 liberated I from 20 c.c. *N*/10 solution. Cl (as NCl) = 15.67.

$C_{11}H_{12}O_2NCl$  requires Cl (as NCl) = 15.71 per cent.

*Acetyl-p-bromoaminopropionophenone*,  $C_2H_5 \cdot CO \cdot C_6H_4 \cdot NBr \cdot CO \cdot CH_3$ , forms brilliant, short, yellow prisms which melt at  $115^{\circ}$ .

0.2704 liberated I from 19.9 c.c. *N*/10 solution. Br (as NBr) = 29.42.

$C_{11}H_{12}O_2NBr$  requires Br (as NBr) = 29.60 per cent.

*Propionyl-p-aminopropionophenone*,  $C_2H_5 \cdot CO \cdot C_6H_4 \cdot NH \cdot CO \cdot C_2H_5$ , crystallises from alcohol in slender, colourless prisms melting at  $153^{\circ}$ ; it is easily soluble in alcohol and chloroform, sparingly so in ligroin.

*Propionyl-p-chloroaminopropionophenone*,  $C_2H_5 \cdot CO \cdot C_6H_4 \cdot NCl \cdot CO \cdot C_2H_5$ , forms colourless, transparent plates and melts at  $80^{\circ}$ .

0.1450 liberated I from 12.1 c.c. *N*/10 solution. Cl (as NCl) = 14.79.

$C_{12}H_{14}O_2NCl$  requires Cl (as NCl) = 14.79 per cent.

*Propionyl-p-bromoaminopropionophenone*,  $C_2H_5 \cdot CO \cdot C_6H_4 \cdot NBr \cdot CO \cdot C_2H_5$ , separates in clusters of pale yellow, elongated plates which melt at  $120^{\circ}$ .

0.1258 liberated I from 8.8 c.c. *N*/10 solution. Br (as NBr) = 27.96.

$C_{12}H_{14}O_2NBr$  requires Br (as NBr) = 28.14 per cent.

*Benzoyl-p-aminopropionophenone*,  $C_2H_5 \cdot CO \cdot C_6H_4 \cdot NH \cdot CO \cdot C_6H_5$ , crys-

callises from alcohol, in which it is sparingly soluble, in thin, colourless, elongated plates melting at  $190^{\circ}$ .

*Benzoyl-p-chloroaminopropiophenone*,  $\text{C}_2\text{H}_5\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{NCl}\cdot\text{CO}\cdot\text{C}_6\text{H}_5$ , crystallises in clusters of colourless, transparent plates melting at  $70^{\circ}$ .

0.1323 liberated I from 9.15 c.c. *N*/10 solution. Cl (as NCl) = 12.25.

$\text{C}_{16}\text{H}_{14}\text{O}_2\text{NCl}$  requires Cl (as NCl) = 12.32 per cent.

*Benzoyl-p-bromoaminopropiophenone*,  $\text{C}_2\text{H}_5\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{NBr}\cdot\text{CO}\cdot\text{C}_6\text{H}_5$ , forms bright yellow, rhombic plates and melts at  $111^{\circ}$ .

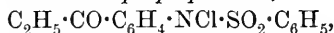
0.1372 liberated I from 8.2 c.c. *N*/10 solution. Br (as NBr) = 23.89.

$\text{C}_{16}\text{H}_{14}\text{O}_2\text{NBr}$  requires Br (as NBr) = 24.07 per cent.

When heated quickly, all the nitrogen halogen derivatives of the acyl *p*-aminopropiophenones undergo transformation at about  $200\text{--}230^{\circ}$ , this change being accompanied by much decomposition.

*Benzenesulphon-p-aminopropiophenone*,  $\text{C}_2\text{H}_5\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_5$ , separates in colourless, glistening plates melting at  $165^{\circ}$ .

*Benzenesulphon-p-chloroaminopropiophenone*,

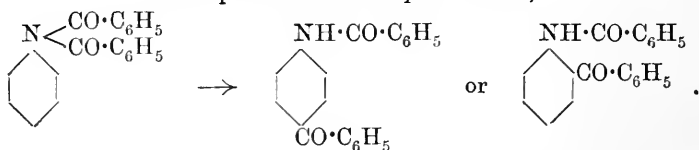


crystallises in colourless, transparent plates which melt at  $81^{\circ}$ .

0.1556 liberated I from 9.2 c.c. *N*/10 solution. Cl (as NCl) = 10.48.

$\text{C}_{15}\text{H}_{14}\text{O}_3\text{NClS}$  requires Cl (as NCl) = 10.95 per cent.

*Transformation of Dibenzanilide into Benzoylo- and -p-aminobenzophenones,*



It was not thought necessary in this case to isolate the dibenzanilide, as this is known to be the first product of the action of benzoyl chloride on benzanilide (*Compt rend.*, 1853, 37, 90; *Ber.*, 1893, 26, 2853). The transformation and isolation of the products are best effected as follows.

The equivalent quantity of benzoyl chloride (2 mols.) is added to aniline (1 mol.) and the whole heated in an oil-bath; the temperature is gradually raised as the interaction takes place, until it reaches  $220\text{--}230^{\circ}$ , at which point it is maintained for about 20 hours. A brown liquid is thus produced, which, on cooling, sets to a viscid, tarry mass. As it is difficult to isolate the isomeric benzoylaminoketones from this, it is best to hydrolyse the whole by dissolving it in a large excess of alcohol mixed with about one-third of its volume of con-

centrated hydrochloric acid. Complete hydrolysis is very difficult to effect, and 14 to 16 hours' boiling is required. After the hydrolysis is complete, steam is blown rapidly through the liquid, when the alcohol first distils over and is followed by a considerable amount of ethyl benzoate. When this has all been removed, the acid liquid is rendered distinctly alkaline with sodium hydroxide, and steam is again passed in; aniline is first expelled and then *o*-aminobenzophenone slowly distils over and either collects as a crystalline solid or separates in bright yellow needles from the cooled distillate. This product is perfectly pure after one crystallisation from alcohol. The para-compound is not volatile in steam and remains behind in the distilling flask; a considerable amount crystallises out on filtering and cooling the hot liquid, and a further quantity can be obtained by repeatedly extracting the tarry residue with very dilute sulphuric acid, from which, on cooling, the base crystallises in a nearly pure state. It can be obtained pure by crystallisation from water containing a few drops of sulphuric acid, in which it dissolves only sparingly, or from alcohol, in which it is readily soluble.

The yields of *o*- and *p*-aminobenzophenones are respectively about 15 per cent. and 45 per cent. of the weight of the aniline used.

As in the analogous transformations of diacetanilide and dipropionanilide, the presence of a little zinc chloride (compare Higgin, Trans., 1882, 41, 132) facilitates the transformation, and a slightly better yield of both isomerides is obtained. The process is carried out in the manner indicated above, about 10 per cent. of finely powdered, dry zinc chloride being added. This process of intramolecular rearrangement, which follows a precisely similar course to the other well-known migrations of groups from the aminic nitrogen atom into the ortho- and para-positions of the ring, could in all probability be carried to the further stage, in which two acyl groups would be introduced into the nucleus in these positions.

Although the use of a larger amount of benzoyl chloride (3 or 4 mols. to 1 mol. of aniline) leads to a somewhat diminished yield of the benzoyl-*o*- and -*p*-aminobenzophenones, which may be due to the occurrence of this additional transformation, yet no disubstituted product has been isolated.

The isomeric change of dibenzanilide is of further interest since it affords the only simple method yet described of preparing *o*-aminobenzophenone, the process described being much less laborious than that employed by Ullmann and Bleier (*Ber.*, 1903, 35, 4273), who converted toluene-*p*-sulphonanthranilic acid into its chloride, and treated benzene with this compound in the presence of aluminium chloride, finally liberating the base by hydrolysis with dilute sulphuric acid.

The following compounds have been prepared from the *o*- and *p*-aminobenzophenones obtained in the foregoing transformation.

The chloroamino- and bromoamino-derivatives of the acylamino-benzophenones were prepared respectively by adding an alcoholic solution of the acylaminoketone to a well-cooled solution of potassium hypochlorite containing an excess of potassium hydrogen carbonate, or to a solution of hypobromous acid containing a little suspended mercuric oxide; the products were then extracted with chloroform and the solution treated as previously described.

*Acetyl-o-chloroaminobenzophenone*,  $C_6H_5 \cdot CO \cdot C_6H_4 \cdot NCl \cdot CO \cdot CH_3$ , separates from a mixture of chloroform and petroleum in brilliant, colourless, flattened prisms with domed ends; it melts at  $102^\circ$ .

0.2022 liberated I from 14.7 c.c. *N*/10 solution. Cl (as NCl) = 12.88.

$C_{15}H_{12}O_2NCl$  requires Cl (as NCl) = 12.96 per cent.

*Acetyl-o-bromoaminobenzophenone*,  $C_6H_5 \cdot CO \cdot C_6H_4 \cdot NBr \cdot CO \cdot CH_3$ , crystallises from a mixture of chloroform and petroleum in short, transparent, yellow prisms melting at  $121^\circ$ .

0.1660 liberated I from 10.5 c.c. *N*/10 solution. Br (as NBr) = 25.28.

$C_{15}H_{12}O_2NBr$  requires Br (as NBr) = 25.13 per cent.

*Propionyl-o-chloroaminobenzophenone*,  $C_6H_5 \cdot CO \cdot C_6H_4 \cdot NCl \cdot CO \cdot C_2H_5$ , crystallises from light petroleum in clusters of colourless, flattened prisms which melt at  $107^\circ$ .

0.1788 liberated I from 12.6 c.c. *N*/10 solution. Cl (as NCl) = 12.49.

$C_{16}H_{14}O_2NCl$  requires Cl (as NCl) = 12.32 per cent.

*Propionyl-o-bromoaminobenzophenone*,  $C_6H_5 \cdot CO \cdot C_6H_4 \cdot NBr \cdot CO \cdot C_2H_5$ , crystallises from light petroleum in bright yellow, transparent plates melting at  $90^\circ$ .

0.1375 liberated I from 8.15 c.c. *N*/10 solution. Br (as NBr) = 23.69.

$C_{16}H_{14}O_2NBr$  requires Br (as NBr) = 24.07 per cent.

*Benzoyl-o-chloroaminobenzophenone*,  $C_6H_5 \cdot CO \cdot C_6H_4 \cdot NCl \cdot CO \cdot C_6H_5$ , separates from light petroleum in colourless, glistening, rhombic plates which melt at  $98^\circ$ .

0.1611 liberated I from 9.7 c.c. *N*/10 solution. Cl (as NCl) = 10.67.

$C_{20}H_{14}O_2NCl$  requires Cl (as NCl) = 10.56 per cent.

*Acetyl-p-chloroaminobenzophenone*,  $C_6H_5 \cdot CO \cdot C_6H_4 \cdot NCl \cdot CO \cdot CH_3$ , crystallises from petroleum (b. p.  $60-80^\circ$ ) in groups of colourless, flattened, elongated plates melting at  $124^\circ$ .

0.2396 liberated I from 17.3 c.c. *N*/10 solution. Cl (as NCl) = 12.79.

$C_{15}H_{12}O_2NCl$  requires Cl (as NCl) = 12.96 per cent.

*Acetyl-p-bromoaminobenzophenone*,  $C_6H_5 \cdot CO \cdot C_6H_4 \cdot NBr \cdot CO \cdot CH_3$ , is less soluble than its analogues in chloroform; it crystallises from a mixture of about 1 part of chloroform and 3 parts of petroleum (b. p. 60—80°) in groups of pale yellow, six-sided plates melting at 151°.

0.1624 liberated I from 10.2 c.c. *N*/10 solution. Br (as NBr) = 25.11.  
 $C_{15}H_{12}O_2NBr$  requires Br (as NBr) = 25.13 per cent.

*Propionyl-p-aminobenzophenone*,  $C_6H_5 \cdot CO \cdot C_6H_4 \cdot NH \cdot CO \cdot C_2H_5$ , crystallises from alcohol in clusters of thin, colourless, elongated plates which melt at 139°. The composition of this and other acyl derivatives is found by the analysis of their chloroamino-derivatives.

*Propionyl-p-chloroaminobenzophenone*,  $C_6H_5 \cdot CO \cdot C_6H_4 \cdot NCl \cdot CO \cdot C_2H_5$ , separates from light petroleum in glistening, colourless, flattened prisms melting at 129°.

0.1730 liberated I from 12 c.c. *N*/10 solution. Cl (as NCl) = 12.29.  
 $C_{16}H_{14}O_2NCl$  requires Cl (as NCl) = 12.32 per cent.

*Propionyl-p-bromoaminobenzophenone*,  $C_6H_5 \cdot CO \cdot C_6H_4 \cdot NBr \cdot CO \cdot C_2H_5$ , crystallises from light petroleum in pale yellow, transparent plates which melt at 123°.

0.1828 liberated I from 11 c.c. *N*/10 solution. Br (as NBr) = 24.06.  
 $C_{16}H_{14}O_2NBr$  requires Br (as NBr) = 24.08 per cent.

*Benzoyl-p-chloroaminobenzophenone*,  $C_6H_5 \cdot CO \cdot C_6H_4 \cdot NCl \cdot CO \cdot C_6H_5$ , separates from petroleum (b. p. 60—80°) in clusters of small, colourless, rhombic plates melting at 107°.

0.2382 liberated I from 14 c.c. *N*/10 solution. Cl (as NCl) = 10.42.  
 $C_{20}H_{14}O_2NCl$  requires Cl (as NCl) = 10.56 per cent.

*Benzoyl-p-bromoaminobenzophenone*,  $C_6H_5 \cdot CO \cdot C_6H_4 \cdot NBr \cdot CO \cdot C_6H_5$ , crystallises from a mixture of chloroform and petroleum in clusters of bright yellow, transparent, rhombic plates and melts at 93°.

0.2288 liberated I from 12 c.c. *N*/10 solution. Br (as NBr) = 20.97.  
 $C_{20}H_{14}O_2NBr$  requires Br (as NBr) = 21.03 per cent.

*Benzenesulphon-p-aminobenzophenone*,  $C_6H_5 \cdot CO \cdot C_6H_4 \cdot NH \cdot SO_2 \cdot C_6H_5$ , crystallises from alcohol in colourless, transparent plates and melts at 156°.

*Benzenesulphon-p-chloroaminobenzophenone*,  
 $C_6H_5 \cdot CO \cdot C_6H_4 \cdot NCl \cdot SO_2 \cdot C_6H_5$ ,  
 separates from a mixture of chloroform and petroleum in colourless, short, flattened prisms which melt at 114°.

0.2969 liberated I from 16 c.c. *N*/10 solution. Cl (as NCl) = 9.55.

$C_{19}H_{14}O_3NClS$  requires Cl (as NCl) = 9.54 per cent.

*Toluene-p-sulphon-p-aminobenzophenone*,



crystallises from alcohol in colourless, thin, flattened prisms melting at 184°.

*Toluene-p-sulphon-p-chloroaminobenzophenone*,



crystallises from a mixture of chloroform and petroleum in clusters of somewhat irregular, colourless plates melting at 116°.

0.3264 liberated I from 16.9 c.c. *N*/10 solution. Cl (as NCl) = 8.97.

$C_{20}H_{16}O_3NClS$  requires Cl (as NCl) = 9.19 per cent.

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## XLIV.—*The Constitution of Phenolphthalein.*

By ARTHUR GEORGE GREEN and ARTHUR GEORGE PERKIN.

THE well-known behaviour of phenolphthalein with alkalis—the production of a deeply-coloured salt from a colourless acid and the disappearance of the colour on the addition of an excess of alkali or of alcohol—is generally explained on the theory of electrolytic dissociation. It is supposed that whilst phenolphthalein itself and its undissociated salts are colourless, its ions are red, and that the disappearance of the colour on adding an excess of alkali or alcohol denotes the suppression or retrogression of ionisation. This view, first put forward by Ostwald (*Wissenschaftl. Grundlagen der Analyt. Chemie*, II<sup>te</sup> Aufl., p. 116), has been adopted by Herzig and Meyer (Herzig, *Ber.*, 1895, 28, 3258; 1896, 29, 138; *Monatsh.*, 1896, 17, 429; 1902, 23, 709; R. Meyer, *Jahrbuch d. Chem.*, 1899, 9, 404) and by O. Fischer (*Zeit. Farb. Text. Chem.*, 1902, 1, 281); whilst quite recently R. Meyer and O. Spendler (*Ber.*, 1903, 36, 2949), after a careful re-examination of the facts, have come to the conclusion that it still offers the best explanation, and that the quinonoid theory does not give a satisfactory solution.

On the other hand, the quinonoid theory of colour has received its strongest experimental support from the work of Nietzki on the ethers of fluorescein, a compound itself closely allied to phenolphthalein, whilst the constantly increasing weight of evidence in general favour

of this theory should lead us to question its lack of application in this case.

With the view of testing the validity of the ionic explanation, we have carried out the following experiments. If the ionisation of the phenolphthalein alkali salt is suppressed by the presence of an excess of free alkali, it appears to follow that the red colour should return if this excess be neutralised. We have found, however, that if an aqueous solution of phenolphthalein containing an excess of caustic potash sufficient to decolorise it (or nearly so) is carefully cooled and gradually neutralised by a weak organic acid, such as acetic or carbonic acid, the solution may be rendered quite neutral without any return of the red coloration. Nor does the colour return on again rendering the solution alkaline. On the other hand, if the solution is acidified and heated or left for some time at the ordinary temperature, then on again rendering alkaline, the colour returns in its full intensity.

In order to ascertain the point at which neutrality occurs, and thereby gain some insight into the nature of the colourless compound present, a weighed quantity of phenolphthalein was dissolved in a measured volume of standard caustic potash sufficient to decolorise it all but a slight pink colour. The solution was cooled in ice and carefully titrated with dilute acetic acid of known strength until neutral to litmus paper. This point exactly coincides with the disappearance of the residual pink colour. The experiment was repeated several times, and it was always found that the quantity of acetic acid required corresponded with the presence in the neutral solution of a potassium salt,  $C_{20}H_{15}O_5K$ .

For example, 0.5 gram of phenolphthalein was dissolved in 10 c.c. of caustic potash solution, of which 1 c.c. = 0.194 gram of KOH and titrated to neutrality with dilute acetic acid, of which 1 c.c. = 0.146 gram  $H_4C_2O_2$ , namely, 14.3 c.c. corresponded with 10 c.c. of the caustic potash solution used. The volume of acetic acid required was 13.65 c.c.

Percentage of KOH neutralised by phenolphthalein.

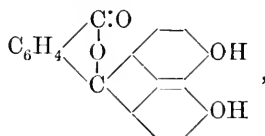
Found	Calculated for $C_{20}H_{15}O_5K$
17.6	17.6

The freshly prepared cold solution of the potassium salt was a clear, colourless liquid which soon became turbid through separation of free phenolphthalein. When rendered alkaline, it only gave a slight pink coloration, but if first allowed to remain until turbidity had set in a more or less intense red was produced. Further, if the colourless neutral solution was simply heated to boiling, it assumed the deep red

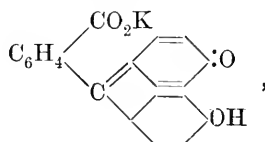
colour of alkaline phenolphthalein, whilst a colourless precipitate of free phenolphthalein separated out. At the same time, the solution is found to have become strongly alkaline to litmus paper. The red colour remains on cooling.

All these facts seem to be quite inconsistent with the electrolytic hypothesis. On the other hand, they are capable of simple explanation by means of the quinonoid theory, according to which the phenomena must be regarded as hydration and dehydration changes accompanied by a transition from the benzenoid to the quinonoid type and *vice versa*.

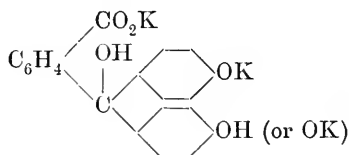
If we assign to free phenolphthalein the usual lactonic constitution,



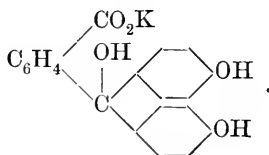
we may assume that the first action of an alkali is to neutralise one of the phenolic hydroxyl groups. The phenolic salt thus formed would be unstable, and may be considered to undergo an immediate rearrangement by the transference of the metal from the phenolic to the carboxylic group. In this way, the red quinonoid salt,



would be formed without intermediate production of the hydrol. On the addition of a further quantity of an alkali, the elements of potassium (or sodium) hydroxide are taken up, giving rise to the colourless compound



If, now, the cooled alkaline solution be neutralised with acetic acid, the metal attached to the phenolic oxygen will be removed and the colourless solution will contain the potassium salt of the carbinol-carboxylic acid,



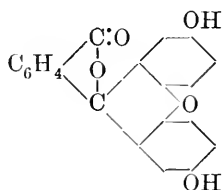
This compound is unstable, and on boiling or when left at the ordinary temperature it undergoes dehydration. This change seems to take place in two directions, partly by formation of the red quinonoid salt, and partly by formation of the colourless lactone. The latter reaction is accompanied by the liberation of potassium hydroxide, which causes the solution to become alkaline. It is, in fact, very probable that the dehydration occurs solely in the second sense, and that the quinonoid compound is only formed from the intermediate lactone by the action of the free alkali simultaneously produced.

We have made many attempts to isolate the colourless carbinol-carboxylic acid (or its salt) in a solid state, but owing to its instability and great solubility in water we have not succeeded in doing so. Nevertheless, there can scarcely be a doubt as to its presence in the neutral colourless solution.

The view of the quinonoid structure of the red salts of phenolphthalein does not, in our opinion, run counter to any of the observed facts. Thus the formation of colourless lactone derivatives by alkylation (Herzig and Meyer) or benzylation (Bistrzycki and Nenki), which have been brought forward as arguments against it, are readily explained if we assume the intermediate formation of the carbinol salt. The difference in the behaviour towards alkalis of phenolphthalein as compared with other triphenylmethane derivatives is only one of degree, and is readily explicable as being due to the presence of the carboxyl group and its tendency to form a lactone with the carbinol hydroxyl group. All the acid colouring matters of the triphenylmethane series (acid violets, acid greens, soluble blues, &c.) are similarly decolorised by an excess of alkali, although with the individual colouring matters there is a large variation in the time required to destroy the colour completely, some requiring only 2 or 3 minutes, whilst others need several days. Even with phenolphthalein, an appreciable time is necessary, which in itself renders the ionisation explanation improbable. The decolorised solutions of the various dyes can be rendered quite neutral by careful addition of acetic acid in the cold without the colour returning, but as soon as the neutral point is passed the colour returns immediately. In the case of erioglaucine, however, the colour does not at once return on acidifying, but only when the solution is heated. This exceptional behaviour is very analogous to that of phenolphthalein, to which erioglaucine may be considered to be similarly constituted, since it contains an  $\text{SO}_3\text{H}$  group instead of a  $\text{CO}_2\text{H}$  group in the ortho-position to the methane carbon atom.

The only difficulty arising from the above view of the constitution of the coloured phenolphthalein salts lies in the behaviour of quinolphthalein, which, according to the researches of R. Meyer and others (R. and H.

Meyer, *Ber.*, 1895, 28, 2959; R. Meyer and L. Friedland, *Ber.*, 1898, 31, 1739; R. Meyer and O. Spendler, *Ber.*, 1903, 36, 2949), has, in the free state, the constitution of a dioxyfluoran:



This compound behaves in a very similar manner to phenolphthalein, although the possibility of a change to a para-quinonoid form is excluded. In order to ascertain whether quinolphthalein exhibits in all respects a completely similar behaviour to phenolphthalein, we have carried out with it the same experiments as recorded above.

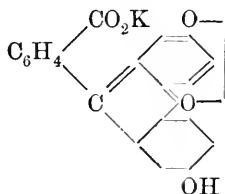
Thus 0.5 gram of quinolphthalein was dissolved in 10 c.c. of caustic potash solution (1 c.c. = 0.194 gram KOH). A violet-red solution was first formed, which quickly became nearly colourless. It was then immersed in a freezing mixture and carefully titrated to neutrality with dilute acetic acid, of which 14.3 c.c. corresponded with 10 c.c. of the caustic potash used; the volume of acetic acid thus required was 13.7 c.c.

Percentage of KOH neutralised by quinolphthalein.

Found	Calculated for $C_{20}H_{13}O_6K$
16.94	16.86

The solution therefore contained the potassium salt of the carbinol-carboxylic acid. The cold neutral solution was quite colourless, but, on heating, the violet-red colour returned, whilst simultaneously the solution became alkaline. The behaviour is therefore exactly similar to that of phenolphthalein.

In order to bring these facts into harmony, we should suggest for the coloured salts of quinolphthalein the ortho-quinonoid structure:



The changes which take place with alkalis would then be represented in a similar manner to those suggested above for phenolphthalein.

Such a view is exactly analogous to that put forward by Kehrman with regard to the constitution of the rosindones and their analogues of the oxazine series.

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# XLV.—Freezing Point Curves of Dynamic Isomerides : Ammonium Thiocyanate and Thiocarbamide.

By ALEXANDER FINDLAY.

NOTWITHSTANDING the importance of many of the substances, comparatively few investigations of the mutual relationships of dynamic isomerides have been carried out from the point of view of the phase rule, and the following short study is therefore offered as a contribution to our knowledge of these (compare Carveth, *J. Physical Chem.*, 1898, 2, 159; 1899, 3, 437; Soch, *ibid.*, 1898, 2, 364; Cameron, *ibid.*, 1898, 2, 409; Hollmann, *Zeit. physikal. Chem.*, 1903, 43, 129).

In the case of all pairs of dynamic isomerides, the different solid forms correspond with a single definite constitution, but in the liquid state, a condition of dynamic equilibrium is established between the two modifications. When, therefore, the fusion and solidification of such substances are studied, the phenomena which are observed will vary according as reversible isomeric transformation takes place with measurable velocity at temperatures in the neighbourhood of the melting points, or only at some higher temperature. The relative velocity of transformation, as compared with the time required to carry out the determination of the melting or freezing point, will also have an influence on the character of the system. If isomeric transformation is relatively rapid, the system will behave like a one-component system, but if the velocity of change is comparatively slow, the behaviour will be that of a two-component system (see Bancroft, *J. Physical Chem.*, 1898, 2, 143; Roozeboom, *Zeit. physikal. Chem.*, 1899, 28, 494). Since it is probable that in all cases the velocity of change can be accelerated by means of catalytic agents, it may be possible to cause a two-component system to behave like a system of one component. This has been effected, for example, in the case of acetaldehyde and paraldehyde (Hollmann, *Zeit. physikal. Chem.*, 1903, 43, 129) by means of sulphuric acid.

If no isomeric transformation takes place in the neighbourhood of

the freezing points, the freezing-point curve obtained will be of the ordinary form exhibited by non-isomeric substances. If, however, isomeric transformation takes place with appreciable velocity, the extent to which these curves will be realised will depend on the velocity with which the change occurs as compared with the rapidity with which the determination of the freezing point can be effected. The general behaviour may be explained with the help of Fig. 1.

If one of the modifications is heated, a temperature will be reached at which it will melt, but this melting point (represented by *A*) will be sharp only if the velocity of isomeric transformation is relatively slow. If the substance is maintained in the fused condition for some time, a certain amount of the isomeric form will be produced, and on lowering the temperature the pure *A*-form will be deposited, not at the temperature of its melting point, but at some lower temperature, depending on the concentration of the *B*-form in the liquid phase. If isomeric transformation takes place slowly in comparison with the rate at which deposition of the solid occurs, the liquid will become increasingly rich in the *B*-modification, and the freezing point will therefore sink continuously until the eutectic point is reached. A similar behaviour will be found if we start with the second isomeric form.

The curve *DE* represents the variation of the equilibrium in the liquid phase with the temperature. This curve may be perpendicular, or may slope either to the right or left, its direction depending on whether or not a heat effect accompanies transformation of the one isomeride into the other (Le Chatelier's Theorem). The point *D* at which this equilibrium curve cuts the freezing-point curve is called the "natural freezing point." This is the only point at which a solid phase (in this case the *A*-modification) can exist in stable equilibrium with the fused mixture (solution), and if isomeric transformation takes place with sufficient rapidity, this is the only freezing point which will be realisable, no matter from which form we start. Evidently, therefore, the degree of completeness with which the freezing point curve can be obtained will depend on the rapidity with which the determinations can be carried out.

Finally, since the natural freezing point is the only temperature at which the system solid—liquid is in stable equilibrium, a little consideration will show that on starting with the pure *B*-form and heating it for varying periods of time so as to cause the formation of the *A*-form, the freezing point which is obtained will first fall until the eutectic point is reached, and then rise until the natural freezing point is attained.

The recent work of Emerson Reynolds and Werner (Trans., 1903, 83, 1) on the equilibrium between ammonium thiocyanate and thiocarb-

amide showed that the velocity of isomeric transformation is comparatively slow at temperatures below about  $140^{\circ}$ . As these investigators did not study the freezing points of ammonium thiocyanate and thiocarbamide, and as they informed me of their intention of not proceeding further with the investigation, the matter seemed to be of sufficient interest and importance to warrant a short study of these isomerides on the lines just laid down, and I now lay the results of this research before the Society.

#### EXPERIMENTAL.

The ammonium thiocyanate and the thiocarbamide employed were obtained from Kahlbaum, and were recrystallised from water, the thiocarbamide being well washed with absolute alcohol. The materials were carefully dried, and the attraction of moisture by the ammonium thiocyanate during the preparation of the mixtures was guarded against by carrying out the operations in a large hot-air chamber. For the determination of the freezing points, about 20 grams of the mixture of thiocarbamide and ammonium thiocyanate were placed in a test-tube fitted with a cork, through which passed a glass stirrer and a thermometer graduated in tenths of a degree. The tube was heated by means of a glycerin bath, also furnished with a stirrer. After the complete liquefaction of the mixture had been effected, the temperature of the bath was allowed to fall slowly, and the determination of the freezing point carried out in the ordinary manner. This determination was made several times with the same quantity of substance, the temperature of the bath being maintained at not more than about  $1^{\circ}$  below the freezing point of the mixture. If the mixture was stirred, surfusion was not found to occur to any great extent (not more than about  $0.5^{\circ}$ ).

In the first set of experiments which were carried out, varying quantities of ammonium thiocyanate and thiocarbamide were intimately mixed, and a portion of the mixture was used for the freezing point determination, whilst the other portion was analysed. The method of analysis was that used by Emerson Reynolds and Werner. In these cases, it was necessary to make sure that incorrect values of the freezing point were not obtained, owing to change occurring in the composition of the mixture through isomeric transformation. A series of freezing point determinations were therefore made with each mixture extending over a period of 30—40 minutes, the times at which the different freezing points were determined being noted. It was found, however, that at temperatures below about  $130^{\circ}$ , the change of the freezing point was very small.

In later experiments, however, the composition of the mixture was

ascertained from samples withdrawn in small tubes from the fused mass, after the freezing point had been determined. In this way, greater certainty was obtained that the composition thus determined corresponded with the particular freezing point. More especially was this method of procedure necessary with mixtures containing as much as 50 per cent. of thiocarbamide, for, in this case, very appreciable alteration of the composition took place at the temperature of the freezing point. By noting the time at which the last freezing point was determined and the time at which the sample was withdrawn, a fairly accurate estimate of the freezing point could be made corresponding with the ascertained composition.

The values of the freezing point obtained are given in the following table, and represented graphically in Fig. 1.

*Freezing Point of Mixtures of Ammonium Thiocyanate and Thiocarbamide.*

Percentage of thiocarbamide.	Freezing point.	Percentage of thiocarbamide.	Freezing point.
9.1	135.5°	30.4	106.2°
12.8	131.0	32.94	105.9
16.6	127.4	35.7	110.5
17.4	124.0	40.2	117.5
22.3	118.2	51.9	131.3
25.9	113.4		

Apart from the numbers given in the table, a series of other determinations were made at different times, which also confirm the course of the curve.

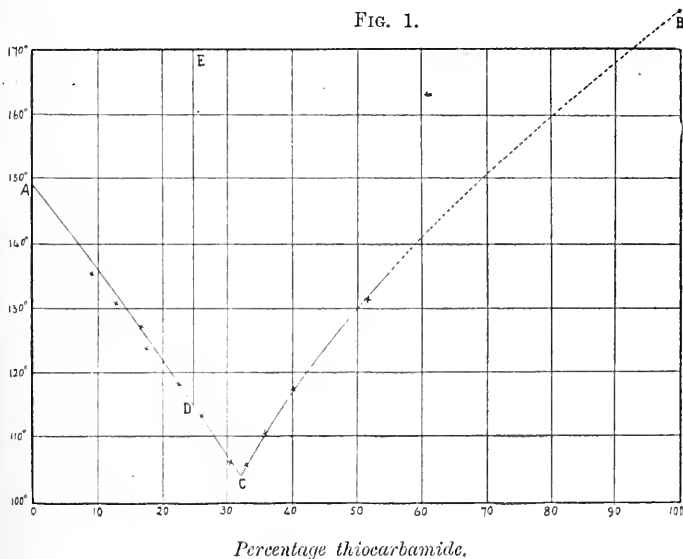
Although the values of the freezing point are given in tenths of a degree, no claim is made that these figures are accurate to less than about 0.5°, and in the case of the higher temperatures the error may be greater.

As is evident from Fig. 1 (p. 407), the freezing point curve of ammonium thiocyanate and thiocarbamide is of the simplest form, indicating the non-formation of a compound between the two components. From all solutions of the composition represented by *AC*, ammonium thiocyanate separates out in the form of crystalline scales. From solutions of the composition represented by *BC*, thiocarbamide separates in fine, crystalline needles, which are quite different in appearance from those of ammonium thiocyanate. By allowing the mixture containing 30 per cent. of thiocarbamide to cool, the eutectic point was found to be 104.5°. This was confirmed in a later experiment.

*Melting Point of Ammonium Thiocyanate and of Thiocarbamide.*

Even at the melting points of these two substances, isomeric transformation can take place with quite appreciable velocity in the case of ammonium thiocyanate, and with very considerable velocity in the case of thiocarbamide. The determination of the melting point, therefore, cannot be carried out with any great degree of accuracy, since the temperature found will depend on the rapidity with which the operation is carried out. By carrying out the determination rapidly, the melting point of ammonium thiocyanate was found to be

FIG. 1.



149°, as also found by other investigators. With regard to thiocarbamide, I believe that the true melting point, if it could be obtained, would be found to lie much higher than 159°, the value given by Emerson Reynolds and Werner, and higher even than 170°, the value given by Prätorius-Seidler (*J. pr. Chem.*, 1880, [ii], 21, 141). This conclusion has been arrived at from determinations of the melting point carried out rapidly in the ordinary apparatus, which yielded values between 172° and 178°. To lessen as far as possible the inaccuracy introduced by too rapid heating, the melting points of the thiocarbamide and of camphor were taken at the same time in the same bath. The camphor was found to melt first. A determination of the melting point of camphor carried out more slowly in the ordinary

manner gave a value  $177^{\circ}$ . The melting point of thiocarbamide is, therefore, probably higher than this.

This conclusion is also supported by the position of the eutectic point; for it is well known that the more nearly coincident are the melting points of two substances, the closer does the eutectic point, as a rule, correspond with the 50 per cent. mixture. Although this rule is only approximately true, one would nevertheless expect that if the melting points of ammonium thiocyanate and thiocarbamide were  $149^{\circ}$  and  $159^{\circ}$  respectively, the eutectic point would correspond with 50 rather than with 30 per cent. of thiocarbamide.

### *Natural Freezing Point.*

The natural freezing point is the point at which the curve of equilibrium in the liquid phase cuts the freezing-point curve. This point could be readily determined if transformation took place with sufficient velocity, since the natural freezing point would then be the temperature at which all mixtures of the two isomerides would freeze. But in the present case, transformation does not occur sufficiently rapidly. If, however, the equilibrium composition is determined at two temperatures, the natural freezing point can be obtained with sufficient accuracy by joining the equilibrium points so determined and prolonging the line downwards to meet the freezing-point curve. In the case of ammonium thiocyanate and thiocarbamide, the equilibrium composition in the fused state has been found both by Waddell (*J. Physical Chem.*, 1898, 2, 525) and by Emerson Reynolds and Werner (*loc. cit.*) to be independent of the temperature, although the value of the equilibrium found by the different investigators was not the same. From the fact that the latter investigators carried out their determination with larger quantities of substance, preference may be given to their value. Moreover, a determination which I also made gave a value agreeing with their result.

Assuming, then, that the equilibrium in the liquid phase at the temperature  $170-180^{\circ}$  occurs when the mixture contains 25 per cent. of thiocarbamide, and also that the equilibrium is not altered by change of temperature, it is evident that the natural freezing point is about  $114-115^{\circ}$ , the stable solid form at this temperature being ammonium thiocyanate. This fact is of interest on account of the difference in behaviour as compared with polymorphous forms of a substance. In the latter case, the more stable form in the neighbourhood of the melting point is that with the higher melting point. Here, however, it is the more fusible form. A similar behaviour has been found in the case of the isomeric benzaldoximes (Cameron, *J. Physical Chem.*, 1898, 2, 409), and, wherever found, it is a sure sign

that isomeric or polymeric, and not polymorphous forms of a substance are being studied.

Finally, from the fact that the equilibrium in the liquid phase is independent of the temperature, the conclusion can be drawn that, in accordance with Le Chatelier's theorem, reciprocal transformation of ammonium thiocyanate and thiocarbamide is not accompanied by any heat effect. This is apparently not unusual in the case of dynamic isomerides, and has been met with in the case of the isomeric benzaldoximes (Cameron, *loc. cit.*) and the isomeric anisaldoximes (Carveth, *J. Physical Chem.*, 1899, 3, 437).

#### *Passage from the Curve BC to AC.*

As has already been pointed out, it should be possible in the case of dynamic isomerides by starting with the less stable form to obtain, on heating, first a fall and then a rise of the freezing point. Hitherto, this had been experimentally verified only in the case of the isomeric benzil-*o*-carboxylic acids (Soch, *J. Physical Chem.*, 1898, 2, 364). It is, however, also found in the case of ammonium thiocyanate and thiocarbamide.

Thiocarbamide was fused and the liquid maintained at a temperature of 160—170° for a certain time, and the freezing point then determined. The temperature was again raised and the freezing point again determined. In this way, the following freezing points were obtained: 108°, 103°, 104°, 105.5°, 106.5°. In the case of the first two determinations, the solid separated out in needle-shaped crystals like thiocarbamide, but in the case of the others, apparently in scales, like ammonium thiocyanate.

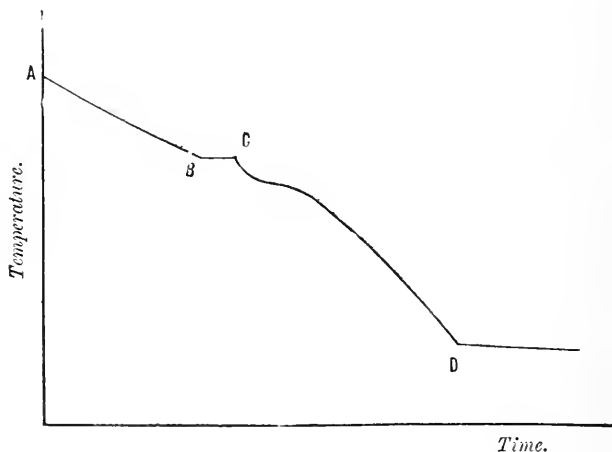
#### *Cooling Curve.*

From the form of the cooling curve of a mixture, valuable conclusions can be drawn with regard to the changes which take place in the system. Indeed, as has recently been emphasised by Tammann (*Zeit. anorg. Chem.*, 1903, 37, 303), it is possible, from a study of the cooling curve and from the "halts" which such a curve exhibits, to get a complete insight into the mutual relations of mixtures of two substances, and to determine the composition of any compounds formed, without the necessity of making a single analysis.

I have therefore supplemented the determinations of the freezing points by ascertaining the form of the cooling curve, starting with a mixture containing about 22 per cent. of thiocarbamide. The curve obtained is shown in Fig. 2 (p. 410). The mixture was first of all fused completely, the temperature thereby rising to about 125°. The tempera-

ture was then allowed to fall slowly, and the rate of cooling noted. So long as only liquid was present, the cooling curve remained continuous as shown by the curve *AB*. The portion *BC*, which ascends slightly, indicates the separation of solid at the freezing point. This is then followed by a rapid fall owing to the temperature of the bath having meanwhile sunk considerably below the temperature of the mixture, whereby rapid separation of the solid phase is caused and a consequent fall in the temperature owing to the increase in the concentration of thiocarbamide in the liquid phase. Cooling then goes on regularly until the eutectic point is reached at which the temperature remained constant ( $104.3^{\circ}$ ) until complete solidification had occurred. This curve, therefore, agrees with the freezing point

FIG. 2.



curve in giving no indication of the formation of a compound  $(\text{NH}_4 \cdot \text{CNS})_3 \cdot \text{CS}(\text{NH}_2)_2$ , since the appearance of such a compound would be indicated by a "break" in the cooling curve between *C* and *D*.

#### *Analysis of the Solid Phase.*

For the purpose of confirming the conclusions which can be drawn from the freezing-point curve as to the non-formation of a compound between ammonium thiocyanate and thiocarbamide, a mixture containing about 27—28 per cent. of the latter isomeride was prepared, completely fused, and allowed to cool down until solid began to separate out. The bath temperature was kept at  $107$ — $108^{\circ}$ , and the solid which separated was filtered off through platinum gauze. On analysis, only about 10 per cent. of thiocarbamide was found. The presence of

this fairly large amount of thiocarbamide is to be accounted for by the difficulty of filtration with the apparatus employed. It is evident, however, that the solid which separated from the fused mixture could not be the compound  $(\text{NH}_4 \cdot \text{CNS})_3 \cdot \text{CS}(\text{NH}_2)_2$ .

### *Stability Limits.*

The term "stability limit" was introduced by Knorr (*Annalen*, 1896, 293, 88) to indicate that temperature above which liquefaction and isomeric change take place. As employed by Knorr and others, however, the term does not have a precise meaning, since it is used to denote not the temperature at which these changes *can* occur, but the temperature at which the change is appreciable, and the introduction of an indefinite velocity of change renders the temperature of the stability limit also indefinite. This indefiniteness has also been recognised by Knorr (*ibid.*, 1899, 306, 334).

Since, however, the stable modification can always undergo isomeric change and liquefy at temperatures above the natural freezing-point, but not below it, and, moreover, since the less stable modification can undergo isomeric transformation and liquefy at temperatures above the eutectic point, but will not liquefy below it, it would appear better, as the author has suggested, to identify the natural freezing point and the eutectic point with the stability limits of the stable and unstable modifications respectively. The opinion expressed by Knorr (*loc. cit.*) that "theoretically" the stability limits of most desmotropic forms, with the exception of enantiomorphous substances, will probably coincide with the melting points, does not appear to me to be justified, since, as stated above, liquefaction and transformation can "theoretically" take place at temperatures below the melting points of either isomeride.

### *Summary.*

1. The freezing-point curve of ammonium thiocyanate (m. p.  $149^\circ$ ) and thiocarbamide (m. p. above  $177^\circ$ ) is of the simplest form, consisting of two branches meeting at a eutectic point ( $104.3^\circ$ ).
2. The natural freezing point is  $114$ — $115^\circ$ , the stable solid form being ammonium thiocyanate.
3. Neither the freezing-point curve, nor the cooling curve, nor the analysis of the solid phase gives any indication of the formation of a compound of ammonium thiocyanate and thiocarbamide stable at temperatures in the neighbourhood of the freezing-point curve.
4. The transformation of ammonium thiocyanate into thiocarbamide and *vice versa* does not appear to be accompanied by any heat effect.

5. The "stability limits" of dynamic isomerides (including desmotropic forms) are defined as the natural freezing point and the eutectic point for the stable and unstable forms respectively.

CHEMICAL DEPARTMENT,  
UNIVERSITY OF BIRMINGHAM.

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## XLVI.—*A Note on Phenylldimethylallylammonium Compounds.*

By ALFRED WILLIAM HARVEY.

The work which forms the subject of this note was commenced some eight months ago, but its completion was unavoidably delayed, and in the meanwhile a paper was published on the subject by H. O. Jones (Trans., 1903, 83, 1400) which contained results differing in some respects from those obtained by the author.

In this investigation, an attempt has been made to prepare and resolve into their optically active components, substituted quaternary compounds containing two similar groups.

Phenylldimethylallylammonium iodide was prepared by mixing molecular proportions of dimethylaniline (48 grams) and allyl iodide (67 grams). After a few days, the semi-solid product was finely ground and filtered, 67 grams of solid phenylldimethylallylammonium iodide being obtained. The impure product, which rapidly deliquesced on exposure to air, was further purified by washing with acetone, the final purification being effected by solution in absolute alcohol and precipitation by the cautious addition of ether. Phenylldimethylallylammonium iodide, when pure, melts at 86–88°, and when crystallised from acetone forms large, pink tables, which were never obtained colourless; the pure substance was not deliquescent.

Phenylldimethylallylammonium *d*-camphorsulphonate was prepared by mixing molecular proportions of the iodide and silver *d*-camphorsulphonate; both constituents were finely powdered before mixing, and the mixture was boiled for one hour in a mixture of equal parts of ethyl acetate and acetone. The precipitated silver iodide was filtered off and the salt, which crystallised very readily, was obtained in six fractions by successive crystallisations. No alcohol was used in the preparation and the product was never gummy. The salt crystallised in fine, colourless needles melting at 156°.

The rotatory power, for sodium light, of each of these fractions, in a two per cent. solution, was found to be the same, and the calculated  $[M]_D$  was identical, within the limits of experimental error, with that

of the activity due to the active acid ion, namely,  $[M]_D + 51.7^\circ$ . It was repeatedly observed that an alteration in the concentration of the solution caused a different value for the specific rotation to be obtained at the same temperature, thus, a 1 per cent. solution gave  $[\alpha]_D + 11.9^\circ$ , whilst a 2 per cent. solution had  $[\alpha]_D + 13.3^\circ$ .

As it was possible that a separation of the dextro- and lævo-isomerides might be effected by crystallisation at a higher temperature, search was made for a suitable solvent having a high boiling point. Pyridine was chosen, as phenyldimethylallylammonium *d*-camphorsulphonate is fairly soluble in this solvent in the cold and readily so at the boiling point. A crop of crystals was thus obtained at about the temperature of boiling water. This fraction was not, however, found to exhibit any optical activity due to the basic ion.

As this substance was found to be very sparingly soluble in ethyl acetate, and as Jones described it as readily soluble in ethyl acetate, its solubility in this solvent was determined and found to be less than 8 parts in 5000 parts of a boiling solution of the salt in ethyl acetate. Four separations of the *d*-camphorsulphonate were obtained by the successive addition of quantities of ethyl acetate to a cold solution of the salt in pyridine, and these four fractions also showed no activity due to the basic ion.

0.2006 gave 0.4697  $\text{CO}_2$  and 0.1423  $\text{H}_2\text{O}$ .  $\text{C} = 63.8$  ;  $\text{H} = 7.8$ .  
 $\text{N}(\text{C}_6\text{H}_5)(\text{CH}_3)_2 \cdot \text{C}_3\text{H}_5 \cdot \text{C}_{10}\text{H}_{15} \cdot \text{O} \cdot \text{SO}_3$  requires  $\text{C} = 64.1$  ;  $\text{H} = 7.8$  per cent.

Phenyldimethylallylammonium platinichloride was obtained as a pale yellow crystalline precipitate on adding the requisite quantity of platinic chloride to an aqueous solution of the final fraction from ethyl acetate and acetone of phenyldimethylallylammonium *d*-camphorsulphonate, acidified with hydrogen chloride. The precipitated salt, which was collected and thoroughly washed with water, when dried in the air, melted at  $162\text{--}165^\circ$  with decomposition.

0.5130 gave 0.1439 Pt.  $\text{Pt} = 26.9$ .

$[\text{N}(\text{C}_6\text{H}_5)(\text{CH}_3)_2 \cdot \text{C}_3\text{H}_5]_2\text{PtCl}_6$  requires  $\text{Pt} = 26.6$  per cent.

A cold aqueous solution of the platinichloride, which is slightly soluble in water, was examined in the polarimeter, but was found to be quite inactive. A further examination was made by suspending about half a gram of the salt in water, slightly acidified with hydrogen chloride ; the platinichloride was then decomposed by passing a current of hydrogen sulphide through the cold solution ; the precipitated platinum sulphide was filtered off and the solution examined in the polarimeter. This solution, also, was found to be inactive.

As Jones has succeeded in obtaining *d*- and *l*-isomerides of phenylbenzylmethylethylammonium salts having optical rotations of similar

arithmetical value (Trans., 1904, 85, 223), the author proposes to revise the work of Pope, Peachey, and himself, who failed to find such a close agreement in the case of the *d*- and *l*-phenylbenzylmethylallylammonium salts.

The author's thanks are due to the Research Fund Committee of the Chemical Society for a grant which defrayed the expenses of this research.

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## XLVII.—*A Note on the Composition of Distilled Oil of Limes and a New Sesquiterpene.*

By HERBERT EDWARD BURGESS and THEODORE HENRY PAGE.

An investigation of terpeneless or concentrated oil of distilled limes\* showed that this product contained about 40 per cent. of free alcohols. The oil was separated by distillation *in vacuo* into two fractions.

(1) The lower fraction, which boiled at about 100—105°/17 mm. and had a sp. gr. 0.930 at 15°, was viscous and retained the distinctive odour of the oil. By repeated fractionation, it was obtained in quantities approximating to those found for the alcohols by direct estimation, and had the following constants: sp. gr. 0.934 at 15°,  $\alpha$ —19°30' (100 mm. tube), and  $n_D$  1.4806 at 20°.

When cooled in a freezing mixture and sown with a crystal of terpeneol, this fraction became nearly solid. After separation and crystallisation from dilute alcohol, the product melted at 35°. In a supercooled state, the substance had the following constants: sp. gr. 0.941 at 15°,  $[\alpha]_D$ —20°, and  $n_D$  1.4829 at 20°; it boiled at 214°/762 mm.

The terpeneol was further characterised by the preparation of certain of its derivatives. Several of these were found to melt a little low, but this is stated to be the case for the derivatives of the active terpeneols as compared with those of the inactive variety.

The nitrosochloride was obtained in practically quantitative yield by adding hydrochloric acid diluted with glacial acetic acid to a well-cooled solution of the terpeneol and amyl nitrite in glacial acetic acid, the product being precipitated with ice-water. After recrystallisation from ethyl acetate, it melted at 105—106°.

\* The oil obtained after distilling off the terpenes.

The nitroleanilide, prepared from the preceding compound by warming with an alcoholic solution of aniline, crystallised from alcohol and melted at 150—151°.

The phenylurethane slowly separated from a mixture of equal volumes of terpineol and phenylcarbimide. After crystallisation from alcohol it melted at 111°.

The terpineol was successively oxidised with 2·5 per cent. potassium permanganate solution and chromic acid mixture (sp. gr. 1·25), the latter reagent being carefully added to the first oxidation product dissolved in a little water. The oil, which separated, solidified after some days, and when recrystallised from water melted at 62°. This product corresponds with the ketolactone from terpineol (m. p. 35°), and was further characterised by conversion into the oxime (m. p. 77°).

These results indicate that laevorotatory terpineol (m. p. 35°) forms a considerable proportion of the oxygenated compounds in distilled oil of limes.

Although the peculiar odour of distilled oil of limes is attached to the terpineol fraction, the terpineol isolated is either practically odourless or has a faint odour of lilac. The aroma is probably due to an isomeric liquid terpineol having a slightly lower boiling point, but at present this supposition is not supported by conclusive evidence.

(2) The second fraction boiled at 130—140°/17 mm., and had a lower sp. gr. than the first, the value of this constant being under 0·900. This fraction was found to give only a slight action with sodium, and hence consisted almost entirely of hydrocarbons, which from their boiling point seemed to be sesquiterpenes. It was diluted with two volumes of dry ether, saturated with hydrogen chloride, and left for several days. On evaporating off the diluent, crystals separated which were collected, and, after crystallisation from ethyl acetate, melted constantly at 79—80°. This product forms colourless crystals readily soluble in ethyl acetate, acetone, or ether, but less so in alcohol, acetic acid, or chloroform; it is characterised by a remarkable power of crystallisation, and is never obtained in an oily state, although its melting point is comparatively low.

The hydrochloride was mixed with  $1\frac{1}{2}$  parts by weight of sodium acetate and 6 parts of acetic acid, and heated nearly to the boiling point for an hour. The crystals first dissolved, but after a time sodium chloride separated. The cooled mixture was then poured into water, washed, and distilled in steam. The dried distillate was fractionated, the last time over sodium, and obtained as a colourless oil with a slight, but peculiar odour; it resinified with great readiness, even when left in a partially filled flask. It boiled at 131° under 9 mm. and at 262—263° (uncorr.) under 756 mm. pressure, in the latter case with slight decomposition; the following constants were

also determined : sp. gr. 0.873 at  $15^\circ$ ,  $[\alpha]_D \pm 0^\circ$ ,  $n_D$  1.4935 at  $15^\circ$ , and 1.4910 at  $19.5^\circ$ ; mol. refract. 68.2, whereas  $C_{15}H_{24}$  (with three double linkings) requires 67.76.

0.2768 gave 0.8970  $CO_2$  and 0.2986  $H_2O$ . C = 88.38; H = 11.99.

$C_{15}H_{24}$  requires C = 88.24; H = 11.76 per cent.

In dilute solution in acetic acid, the hydrocarbon combined with approximately 6 atoms of bromine.

The hydrochloride gave Cl = 34.2.

$C_{15}H_{24}, 3HCl$  requires 34.0 per cent.

This was the only derivative successfully prepared. The nitroschloride, nitrite, bromide, and acetate were unsatisfactory.

From the above data, it seems apparent that distilled oil of limes contains a sesquiterpene, not hitherto described, and differing materially from the other members of the series, especially in specific gravity, which is much lower than the usual value for sesquiterpenes, but approximates to those found for olefinic or partially olefinic sesquiterpenes.

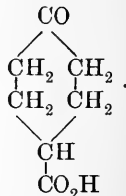
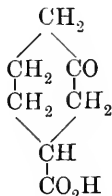
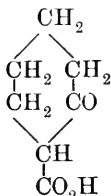
The name "*limene*" is suggested for this sesquiterpene, as having first been found in oil of limes.

Limene is also present in hand-pressed lime oil and in lemon oil in the fraction boiling between  $120^\circ$  and  $140^\circ$  under 9 mm. pressure. The characteristic hydrochloride (m. p.  $79-80^\circ$ ) was readily obtained by saturating this fraction with hydrogen chloride. Other oils of this series are being examined with the view of ascertaining whether limene is present or not.

### XLVIII.— $\delta$ -Ketohehexahydrobenzoic Acid.

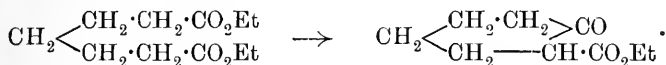
By WILLIAM HENRY PERKIN, jun.

OF the three possible ( $\beta$ -,  $\gamma$ -, and  $\delta$ -)-ketohehexahydrobenzoic (*cyclohexanonecarboxylic*) acids,

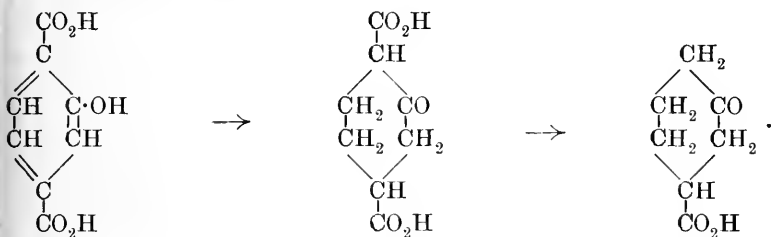


only the first two are known. The ester of the  $\beta$ -acid was synthesised

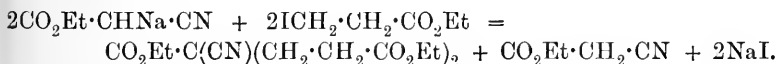
by Dieckmann (*Ber.*, 1894, 27, 103; 1900, 33, 2683) from ethyl pimelate by the action of sodium:



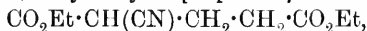
$\gamma$ -Keto-hexahydrobenzoic acid was obtained by Baeyer and Tutein (*Ber.*, 1889, 22, 2182) by first reducing hydroxyterephthalic acid to keto-hexahydroterephthalic acid and then eliminating carbon dioxide by boiling with water:



Since the unknown  $\delta$ -keto-acid might be expected to exhibit unusually interesting properties, the author has been engaged for some time in devising a method for its synthesis, and has ultimately succeeded in preparing it in considerable quantities by the following series of reactions. When ethyl  $\beta$ -iodopropionate and ethyl sodio-cyanoacetate are allowed to interact in molecular proportions at the ordinary temperature, a curious reaction takes place, which results in the formation of ethyl  $\gamma$ -cyanopentane- $\alpha\gamma\epsilon$ -tricarboxylate and regeneration of half of the ethyl cyanoacetate:

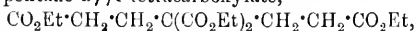


Under the conditions employed, it was to be expected that the mono-substitution product, ethyl  $\alpha$ -cyanopropane- $\alpha\gamma$ -dicarboxylate,



would be formed, but no trace of this substance could be isolated, the reaction proceeding apparently quantitatively in the direction shown above.\* Ethyl cyanopentane-tetracarboxylate is hydrolysed by boiling with concentrated hydrochloric acid with the formation of pentane- $\alpha\gamma\epsilon$ -tricarboxylic acid,  $\text{CO}_2\text{H} \cdot \text{CH}(\text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H})_2$ , which

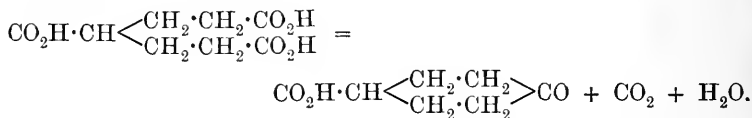
\* In the case of the very similar action of ethyl  $\beta$ -bromopropionate on ethyl sodiomalonate, Emery (*Ber.*, 1891, 24, 282) showed that the principal product of the reaction was the normal mono-substitution product, namely, ethyl propane- $\alpha\gamma$ -tricarboxylate,  $\text{CO}_2\text{Et} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{CO}_2\text{Et})_2$ , but he also noticed that small quantities of ethyl pentane- $\alpha\gamma\epsilon$ -tetracarboxylate,



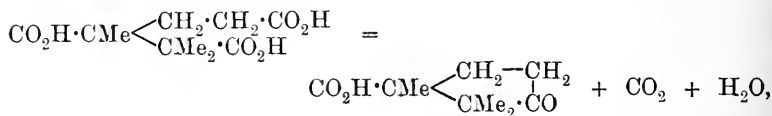
were produced at the same time.

melts at 116—118°, and has already been described by Emery (*Ber.*, 1891, 24, 384) and by Bottomley and Perkin (*Trans.*, 1900, 77, 299).

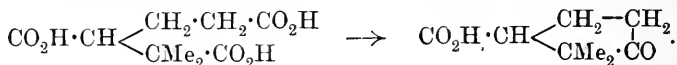
When the sodium salt of this acid is heated with acetic anhydride, or when the acid itself is digested with acetic anhydride and then distilled, a remarkable decomposition takes place with elimination of carbon dioxide and water and formation of  $\delta$ -keto $\delta$ hexahydrobenzoic acid (m. p. 68°):



Similar cases of ring formation from dibasic acids have already been observed on one or two occasions, thus Lapworth and Chapman (*Trans.*, 1900, 77, 464) showed that homocamphoronic acid, when slowly distilled, is converted into camphoronic acid,



and Perkin and Thorpe (*Trans.*, 1904, 85, 138) recently obtained ketodimethylpentamethylenecarboxylic acid by heating the sodium salt of dimethylbutanetricarboxylic acid with acetic anhydride:

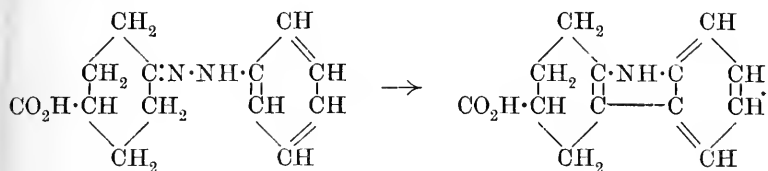


Experiments are in progress, which, it is hoped, will indicate to what extent this valuable method may be employed in the formation of closed chain compounds containing the keto-group.

$\delta$ -Keto $\delta$ hexahydrobenzoic acid crystallises with 1 molecule of water and shows all the properties of a keto-acid; it yields the following derivatives, the preparation and properties of which are described in the experimental part of this paper: *methyl  $\delta$ -keto $\delta$ hexahydrobenzoate*,  $\text{CO}(\text{CH}_2 \cdot \text{CH}_2)_2\text{CH} \cdot \text{CO}_2\text{Me}$  (b. p. 140°/20 mm.); *ethyl  $\delta$ -keto $\delta$ hexahydrobenzoate*,  $\text{CO}(\text{CH}_2 \cdot \text{CH}_2)_2\text{CH} \cdot \text{CO}_2\text{Et}$  (b. p. 158°/40 mm.);  *$\delta$ -ketoxime $\delta$ hexahydrobenzoic acid*,  $(\text{OH})\text{N} \cdot \text{C}(\text{CH}_2 \cdot \text{CH}_2)_2\text{CH} \cdot \text{CO}_2\text{H}$  (m. p. 147°); the *semicarbazone*,  $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{N} \cdot \text{C}(\text{CH}_2 \cdot \text{CH}_2)_2\text{CH} \cdot \text{CO}_2\text{H}$  (m. p. 194°).

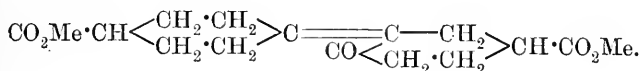
When treated with phenylhydrazine,  $\delta$ -keto $\delta$ hexahydrobenzoic acid yields a yellow oil, which is doubtless the hydrazone, and this, when boiled with hydrochloric acid, loses ammonia and is converted into a sparingly soluble crystalline substance having the formula  $\text{C}_{13}\text{H}_{13}\text{O}_2\text{N}$ . This decomposition is evidently analogous to the well-known conversion of phenylhydrazones into indole derivatives discovered by Emil

Fischer, and the substance  $C_{13}H_{13}O_2N$  is obviously *tetrahydrocarbazole-p-carboxylic acid*, formed according to the scheme :



It is interesting to observe that Baeyer and Tutein (*Ber.*, 1889, 22, 2184) had previously described the exactly similar conversion of  $\gamma$ -keto-hexahydrobenzoic acid into tetrahydrocarbazole-*m*-carboxylic acid by the action of phenylhydrazine and subsequent treatment with hydrochloric acid.

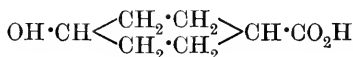
*Carboxyhexamethenyl- $\delta$ -keto-hexahydrobenzoic Acid.*—During a series of experiments on the preparation of the methyl and ethyl esters of  $\delta$ -keto-hexahydrobenzoic acid (see above) it was noticed that, when the acid was boiled with methyl alcohol and sulphuric acid, a large quantity of an oil was formed which, on account of its high boiling point ( $255^\circ$  under 20 mm. pressure), was evidently a condensation product. The examination of this oil proved that it was *methyl carboxyhexamethenyl- $\delta$ -keto-hexahydrobenzoate*, formed by the elimination of water from two molecules of methyl  $\delta$ -keto-hexahydrobenzoate, and therefore its constitution is obviously that represented by the formula :



On hydrolysis, this methyl ester yields the free *carboxyhexamethenyl- $\delta$ -keto-hexahydrobenzoic acid*, a colourless, crystalline substance which melts at  $170^\circ$ . Although it is well known that ketopolymethylene ring compounds readily condense with substances containing the  $>\text{CO}$  group, no case, like the above, seems to have been observed in which condensation of two molecules of the substance is brought about simply by boiling with methyl alcohol and sulphuric acid.

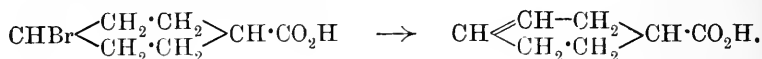
*Reduction of  $\delta$ -Keto-hexahydrobenzoic Acid. Formation of  $\delta$ -Hydroxy-hexahydrobenzoic Acid and the Conversion of this Acid into  $\Delta^3$ -Tetrahydrobenzoic Acid.*

$\delta$ -Keto-hexahydrobenzoic acid is readily reduced by sodium amalgam with formation of  *$\delta$ -hydroxy-hexahydrobenzoic* (cyclohexanol-4-carboxylic) acid,

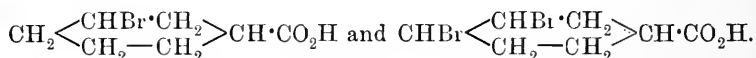


(m. p.  $121^\circ$ ), and, since this acid shows no tendency to form a lactone, it is evidently the *trans*-modification. It was to be expected that both the *cis*- and *trans*-forms of this acid would be produced by the reduction of the keto-acid, but, although a careful search was made, no trace of the *cis*-acid could be isolated.

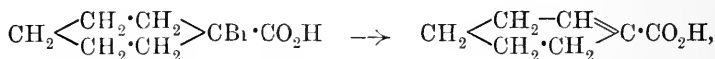
When the hydroxy-acid is heated with hydrobromic acid, it is converted into  $\delta$ -bromohexahydrobenzoic (bromocyclohexane-4-carboxylic) acid (m. p.  $167^\circ$ ), and this, when digested with sodium carbonate, readily loses hydrogen bromide with formation of  $\Delta^3$ -tetrahydrobenzoic ( $\Delta^3$ -cyclohexenecarboxylic) acid,



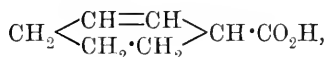
This new acid melts at about  $13^\circ$  and distils at  $237^\circ$  (748 mm.); it shows all the properties of an unsaturated acid, since it reduces permanganate, combines with hydrogen bromide yielding  $\gamma$ -bromohexahydrobenzoic acid (m. p.  $122^\circ$ ), and at once decolorises bromine with formation of  $\gamma\delta$ -dibromohexahydrobenzoic (3:4 dibromocyclohexanecarboxylic) acid (m. p.  $86^\circ$ ),



The above synthesis of  $\Delta^3$ -tetrahydrobenzoic acid is a welcome addition to our knowledge of the chemistry of the tetrahydrobenzoic acids, since all the possible isomerides have now been prepared and carefully investigated. The  $\Delta^1$ -acid (m. p.  $29^\circ$  and b. p.  $240$ – $243^\circ$ ) was obtained by Aschan (*Annalen*, 1892, 271, 267) from bromohexahydrobenzoic acid by elimination of hydrogen bromide,



whereas the  $\Delta^2$ -acid (b. p.  $235^\circ$ ),



is formed by the direct reduction of benzoic acid with sodium amalgam (Hermann, *Annalen*, 1864, 132, 75; Aschan, *loc. cit.*, p. 236).

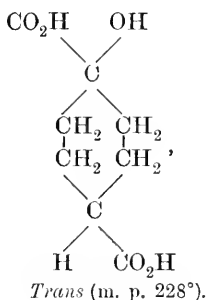
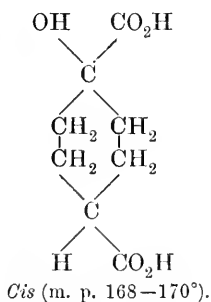
#### *Action of Hydrogen Cyanide on $\delta$ -Keto-hexahydrobenzoic Acid.*

*Formation of the cis- and trans-Modifications of  $\alpha$ -Hydroxyhexahydroterephthalic Acid and of  $\Delta^1$ -Tetrahydroterephthalic Acid.*

When  $\delta$ -keto-hexahydrobenzoic acid is treated with hydrogen cyanide in the presence of potassium cyanide (compare Lapworth, *Trans.*, 1903,

83, 995), addition takes place readily with formation of an oil, which consists of the mixed nitriles of the *cis*- and *trans*-modifications of  $\alpha$ -hydroxyhexahydroterephthalic acid, and from which the *trans*-nitrile (m. p.  $140^\circ$ ) was isolated in a crystalline condition.

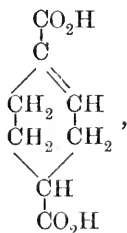
By hydrolysing the mixed nitriles under the conditions described in the experimental part of this paper (p. 435), the corresponding hydroxy-acids,



were easily separated in a state of purity. In the absence of definite proof of their configurations, the more sparingly soluble and less fusible isomeride was taken as being the *trans*-modification.

It is remarkable that when  $\delta$ -ketohehexahydrobenzoic acid is reduced, that is, when the keto-group,  $>\text{CO}$ , is converted into  $>\text{CH}\cdot\text{OH}$ , only one modification of hydroxyhexahydrobenzoic acid should result, whereas, in the very similar addition of hydrogen cyanide, converting the keto-group into  $>\text{C}(\text{CN})\cdot\text{OH}$ , both the *cis*- and *trans*-modifications of the nitrile of  $\alpha$ -hydroxyhexahydroterephthalic acid should be formed. It is also interesting that in the latter case very much more of the *cis*-modification is produced than of the *trans*-modification.

Both the *cis*- and *trans*-modifications of hydroxyhexahydroterephthalic acid are decomposed on distillation, with loss of water and formation of  $\Delta^1$ -tetrahydroterephthalic acid,

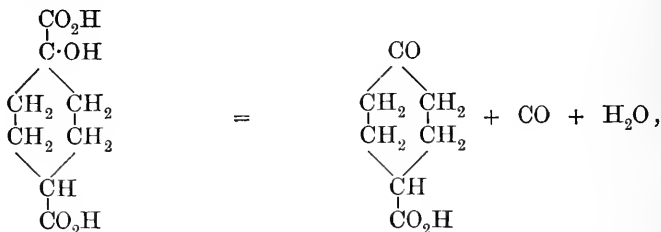


and the acid thus synthesised is identical with the  $\Delta^1$ -tetrahydroterephthalic acid which Baeyer (*Annalen*, 1888, 245, 160) obtained directly from terephthalic acid by reduction with sodium amalgam.

The *cis*- and *trans*-modifications of  $\alpha$ -hydroxyhexahydroterephthalic

acid are readily acted on by concentrated sulphuric acid, decomposition taking place in both cases in two distinct directions.

Part of the acid is decomposed with elimination of carbon monoxide and water and formation of  $\delta$ -keto-hexahydrobenzoic acid,



whereas the remainder is converted into  $\Delta^1$ -tetrahydroterephthalic acid by the simple elimination of water.

The investigation of  $\delta$ -keto-hexahydrobenzoic acid and its derivatives is being continued in various directions.

#### EXPERIMENTAL.

*Ethyl  $\gamma$ -Cyanopentane- $\alpha\gamma\epsilon$ -tricarboxylate,*



In preparing this cyano-ester, the quantities usually employed were sodium (25 grams), alcohol (400 c.c.), ethyl cyanoacetate (125 grams), and ethyl  $\beta$ -iodopropionate\* (250 grams).

The sodium is dissolved in the alcohol in a two-litre flask, and, after cooling, the ethyl cyanoacetate added all at once; the flask is then cooled again in running water and the ethyl  $\beta$ -iodopropionate added in three portions, care being taken that the temperature never rises above  $25^\circ$ , as otherwise some of the ethyl  $\beta$ -iodopropionate is liable to be decomposed with formation of ethyl acrylate (compare *Trans.*, 1904, 85, 120). After being left overnight, the mixture is heated for half an hour on the water-bath, diluted with three times its volume of water, and extracted three times with ether.

The ethereal solution is washed until free from alcohol, dried over

\* Owing to the costliness of  $\beta$ -iodopropionic acid, a number of comparative experiments were made with the object of discovering the best conditions for converting it into its ethyl ester, and the following process was found to give excellent results. The acid (500 grams) is dissolved in alcohol (400 c.c.) and mixed with a cold solution of sulphuric acid (150 grams) in alcohol (200 c.c.) and the whole allowed to remain for four days at the ordinary temperature. The product, which will have separated into two layers, is mixed with three volumes of water, extracted twice with ether, the ethereal solution washed with water containing a little sulphurous acid (to remove iodine), and fractionated under reduced pressure.

The boiling point is  $136^\circ$  under 100 mm. pressure, and the yield 525—535 grams, or 94 per cent. of that theoretically possible.

calcium chloride, and evaporated, and the residual oil fractionated under 20 mm. pressure. At first, unchanged ethyl cyanoacetate passes over, then the temperature rises rapidly to  $220^{\circ}$ , almost the whole of the residue passing over between this and  $240^{\circ}$ ; on repeating the fractionation, the pure substance is then easily obtained, distilling almost constantly at  $228^{\circ}$  (20 mm.).

0.1888 gave 0.3881  $\text{CO}_2$  and 0.1245  $\text{H}_2\text{O}$ .  $\text{C} = 57.0$ ;  $\text{H} = 7.4$ .

0.2880 „ 12.3 c.c. nitrogen at  $15^{\circ}$  and 756 mm.  $\text{N} = 4.9$ .

$\text{C}_{15}\text{H}_{23}\text{O}_6\text{N}$  requires  $\text{C} = 57.5$ ;  $\text{H} = 7.3$ ;  $\text{N} = 4.5$  per cent.

*Ethyl cyanopentanetricarboxylate* is a viscid, colourless oil, which, when placed in a freezing mixture, showed no signs of solidifying.

It is formed apparently quantitatively, according to the equation, given in the introduction (p. 417), since on one occasion, when four of the above quantities were worked up together, the yields obtained were ethyl cyanoacetate (190 grams), and ethyl cyanopentanetricarboxylate (680 grams), whereas the theoretical quantities are 240 and 686 grams respectively.

*Pentane- $\alpha\gamma$ -tricarboxylic Acid*,  $\text{CO}_2\text{H}\cdot\text{CH}(\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$ .

Ethyl cyanopentanetricarboxylate is with difficulty completely hydrolysed by boiling with mineral acids, especially when the operation is carried out in a reflux apparatus, and the alcohol formed cannot escape. This behaviour caused great difficulties at first, and a number of experiments had to be made before the best conditions for hydrolysis were discovered; now that these have been determined, the yield of acid is almost quantitative.

The pure cyano-ester (100 grams) is mixed with concentrated hydrochloric acid (200 c.c.) in a litre flask fitted with a ground-in air condenser, and carefully heated just to boiling on a sand-bath.

In the course of about half an hour, the oil will have completely dissolved, and care is necessary at this stage to avoid loss owing to frothing due to the elimination of carbon dioxide. After 1 hour, the air-tube is removed and the alcohol allowed to escape, a further quantity of hydrochloric acid (50—100 c.c.) is added, and the boiling continued in the open flask for 8 hours. The crystals of pentanetricarboxylic acid mixed with ammonium chloride, which will have separated overnight, are collected at the pump, washed with concentrated hydrochloric acid, and the filtrate again boiled in an open flask, when a further crop of crystals will be obtained. These are treated in the same way as the first crop, and the boiling of the filtrate and the whole cycle of operations continued as long as crystals continue to separate. The last mother liquors, which have a brown colour, are evaporated on the water-bath and the viscid syrup set aside to crystal-

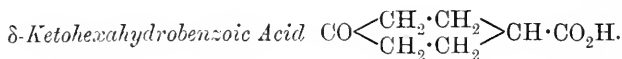
lise; the crude acid is then placed in contact with porous porcelain, when in the course of a few days it will have become almost white. The crops of crystals are combined, thoroughly dried on the water-bath, powdered, and extracted with pure ether,\* preferably in a Soxhlet apparatus, by which means the acid is dissolved, and separated from the insoluble ammonium chloride. The concentrated ethereal solution deposits the pure acid in crystalline crusts, which are collected and washed with ether, and from the mother liquors the remainder of the acid is obtained by concentrating and recrystallising either from ether or from hydrochloric acid.

0.1627 gave 0.2801  $\text{CO}_2$  and 0.0874  $\text{H}_2\text{O}$ .  $\text{C} = 47.0$ ;  $\text{H} = 6.0$ .

$\text{C}_8\text{H}_{12}\text{O}_6$  requires  $\text{C} = 47.1$ ;  $\text{H} = 5.9$  per cent.

*Pentane- $\alpha,\gamma,\epsilon$ -tricarboxylic acid* melts at  $116\text{--}118^\circ$ , and has already been prepared by Emery (*Ber.*, 1891, 24, 284) from ethyl pentanetetracarboxylate,  $(\text{CO}_2\text{Et})_2\text{C}(\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et})_2$ , and by Bottomley and Perkin (*Trans.*, 1900, 77, 299) from ethyl pentanehexacarboxylate,  $(\text{CO}_2\text{Et})_2\text{CH}\cdot\text{CH}_2\cdot\text{C}(\text{CO}_2\text{Et})_2\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{Et})_2$ , by hydrolysis, but the previously observed melting points were rather too low.

The process given in this paper is by far the most suitable for the preparation of large quantities of this acid.



This acid may be obtained in a variety of ways from pentanetricarboxylic acid, as, for example, by the distillation of the ammonium salt or, better, by heating the sodium salt with acetic anhydride under exactly the same conditions as those described in the preparation of ketodimethylpentamethylenecarboxylic acid from dimethylbutanedicarboxylic acid (*Trans.*, 1904, 85, 138), but, as the result of a large number of experiments, the following process, which should be followed exactly, was found to give by far the most satisfactory results. The pure tribasic acid, in quantities of not more than 15 grams, is heated with twice its weight of acetic anhydride for 6 hours, the acetic acid and excess of acetic anhydride are then distilled off, the heating being continued until a thermometer, immersed in the liquid, registers  $180^\circ$ .

The residue is then transferred to a distilling flask connected with the pump and heated in a metal-bath under 15 mm. pressure, the thermometer being in the liquid during the first stages of the opera-

\* It is important that the acid should be heated until every trace of hydrogen chloride has been removed and the ether quite free from alcohol; otherwise, partial etherification takes place and the acid does not crystallise.

tion. Some acetic anhydride passes over, and when the temperature reaches 200—210°, at which it is kept for 10 minutes, carbon dioxide is evolved and the pressure rises. The operation is suspended until the pressure is again reduced to 15 mm., when the heating at 220° is continued and, as soon as the evolution of carbon dioxide is seen to slacken considerably, the thermometer is drawn up to the usual position and the contents of the flask rapidly distilled until the temperature rises to 250°, the considerable brown residue remaining in the flask being neglected.

The distillate, which from 15 grams of tribasic acid weighs about 7 grams, is dissolved in a little water, mixed with semicarbazide hydrochloride (5 grams) and sodium acetate (5 grams), and heated just to boiling. After remaining overnight, the sparingly soluble semicarbazone (p. 427) is collected, washed with water, dissolved in hot dilute hydrochloric acid, and repeatedly extracted with ether. On evaporating the ethereal solution, a pale yellow oil is obtained which solidifies completely on cooling and consists of practically pure  $\delta$ -keto-hexahydrobenzoic acid.

This is the most direct way, if small quantities only of the keto-acid are required, but in preparing the large quantities employed in this research the following method of purification was found to be more convenient and economical.

The distillate from the decomposition of 50 grams of the tribasic acid is fractionated under reduced pressure (15 mm.), when a large fraction passes over at 200—225°, leaving a viscid, brown residue in the flask. On refractionating, practically the whole distils at 205—215° under the same pressure and solidifies almost completely on cooling, and the acid thus obtained, after remaining in contact with porous porcelain for a few days, is pure enough for most purposes, and in this form\* it was, unless otherwise stated, used in the experiments described in this paper. For the analysis, the acid was purified by conversion into the semicarbazone and then recrystallised from a mixture of benzene and light petroleum.

0.1711 gave 0.3689  $\text{CO}_2$  and 0.1092  $\text{H}_2\text{O}$ . C = 58.8; H = 7.1.

0.1523 „ 0.3288  $\text{CO}_2$  „ 0.0960  $\text{H}_2\text{O}$ . C = 58.8; H = 7.0.

$\text{C}_7\text{H}_{10}\text{O}_3$  requires C = 59.1; H = 7.0 per cent.

*$\delta$ -Keto-hexahydrobenzoic acid* melts at about 67—68° with a slight previous softening, and is readily soluble in alcohol, ether, or benzene, but sparingly so in light petroleum; it dissolves readily in cold water, and is soluble in almost all proportions in hot water, from which it separates, on cooling, in magnificent groups of needles.

\* When purified in this way, the yield of keto-acid from 1 kilo. of ethyl  $\beta$ -iodo-propionate varied, in different experiments, from 130—160 grams.

The crystals thus obtained were dried at  $40^\circ$  and found to contain one molecule of water of crystallisation.

0.1782 gave 0.3433  $\text{CO}_2$  and 0.1176  $\text{H}_2\text{O}$ .  $\text{C} = 52.5$ ;  $\text{H} = 7.3$ .

$\text{C}_7\text{H}_{10}\text{O}_3 \cdot \text{H}_2\text{O}$  requires  $\text{C} = 52.5$ ;  $\text{H} = 7.5$  per cent.

The direct determination of the water of crystallisation was difficult, owing to the fact that the acid is slightly volatile at  $100^\circ$ , but, after heating at  $80^\circ$  until practically constant, 0.5096 gram lost 0.0592 gram, or 11.5 per cent., whereas the formula  $\text{C}_7\text{H}_{10}\text{O}_3 \cdot \text{H}_2\text{O}$  requires 11.3 per cent. of water. On titration, 0.2177 of the crystals neutralised 0.0539  $\text{NaOH}$ , whereas this amount of an acid,  $\text{C}_7\text{H}_{10}\text{O}_3 \cdot \text{H}_2\text{O}$ , should neutralise 0.0544 of the alkali.

*Formation of  $\delta$ -Ketohehexahydrobenzoic Acid from the Sodium Salt of Pentane- $\alpha\gamma\epsilon$ -tricarboxylic Acid by the Action of Acetic Anhydride, and from the Ammonium Salt by Distillation.*

In the first experiment, the pure tribasic acid (41 grams) was dissolved in water, mixed with sodium carbonate (33 grams), and evaporated to dryness; the dry salt was powdered and passed through a fine sieve and then heated with acetic anhydride at  $165^\circ$  for 4 hours, when large quantities of carbon dioxide were eliminated.

The product was dissolved in water, mixed with semicarbazide hydrochloride (20 grams), when, after two days, a cake of the semicarbazone of  $\delta$ -ketohehexahydrobenzoic acid had separated, and this was found to weigh 7 grams.

In the second experiment, 14 grams of the pure acid were dissolved in excess of ammonia and evaporated to dryness. The viscid semi-solid mass was first heated under the ordinary pressure, when a quantity of ammonia and steam was given off and, as soon as the temperature of the liquid had risen to  $150^\circ$ , the whole was transferred to the vacuum distillation apparatus and the heating continued under 20 mm. pressure. The mass soon solidified completely, then melted again and gave off a quantity of gas, and much oil distilled over. The distillate, on treatment with semicarbazide hydrochloride and sodium acetate, yielded 3 grams of the semicarbazone of  $\delta$ -ketohehexahydrobenzoic acid.

*The Methyl and Ethyl Esters, the Oxime, and the Semicarbazone of  $\delta$ -Ketohehexahydrobenzoic Acid.*

*Methyl  $\delta$ -Ketohehexahydrobenzoate*,  $\text{CO}(\text{CH}_2 \cdot \text{CH}_2)_2\text{CH} \cdot \text{CO}_2\text{Me}$ .—A quantity of this ester was prepared by digesting the keto-acid with methyl alcohol and sulphuric acid in the usual way, but the yield was

very poor owing to the formation of considerable quantities of methyl carboxyhexamethenylketohexahydrobenzoate (see p. 429).

It is a colourless oil which boils at  $140^\circ$  under 20 mm. pressure.

0.1824 gave 0.4089  $\text{CO}_2$  and 0.1295  $\text{H}_2\text{O}$ .  $\text{C} = 61.2$ ;  $\text{H} = 7.9$ .

$\text{C}_8\text{H}_{12}\text{O}_3$  requires  $\text{C} = 61.5$ ;  $\text{H} = 7.7$  per cent.

*Ethyl  $\delta$ -Keto-hexahydrobenzoate*,  $\text{CO}(\text{CH}_2\cdot\text{CH}_2)_2\text{CH}\cdot\text{CO}_2\text{Et}$ .—This ester may be obtained, in an almost quantitative yield, by digesting the keto-acid (10 grams) with 40 grams of a 3 per cent. solution of hydrogen chloride in absolute alcohol in a reflux apparatus for 6 hours. The product is mixed with 3 times its volume of ether, water is then added, and the ethereal solution separated and washed 3 times with water and once with dilute sodium carbonate.

After drying over calcium chloride and distilling off the ether, an oil is obtained which distils almost constantly at  $158^\circ$  (40 mm.), and consists of pure ethyl  $\delta$ -keto-hexahydrobenzoate.

0.1417 gave 0.3279  $\text{CO}_2$  and 0.1061  $\text{H}_2\text{O}$ .  $\text{C} = 63.1$ ;  $\text{H} = 8.3$ .

$\text{C}_9\text{H}_{14}\text{O}_3$  requires  $\text{C} = 63.5$ ;  $\text{H} = 8.2$  per cent.

*$\delta$ -Ketoximehexahydrobenzoic Acid*,  $(\text{OH})\text{N}:\text{C}(\text{CH}_2\cdot\text{CH}_2)_2\text{CH}\cdot\text{CO}_2\text{H}$ .—In preparing this oxime, the pure acid (2 grams) was dissolved in a little water, mixed with a strong solution of hydroxylamine hydrochloride (2 grams) and caustic potash (4 grams), and after remaining for 2 days, the product was acidified and extracted at least 15 times with ether. The ethereal solution was dried over calcium chloride and evaporated, and the viscid, oily residue, which gradually became semi-solid, left in contact with porous porcelain until quite dry. The substance was then dissolved in ether and the ethereal solution evaporated to a small bulk, when, on cooling, the oxime gradually separated in crystalline crusts.

0.1704 gave 0.3336  $\text{CO}_2$  and 0.1080  $\text{H}_2\text{O}$ .  $\text{C} = 53.4$ ;  $\text{H} = 7.0$ .

0.2014 „ 14.8 c.c. nitrogen at  $11^\circ$  and 748 mm.  $\text{N} = 8.6$ .

$\text{C}_7\text{H}_{11}\text{NO}_3$  requires  $\text{C} = 53.5$ ;  $\text{H} = 7.0$ ;  $\text{N} = 8.9$  per cent.

*$\delta$ -Ketoximehexahydrobenzoic acid*, melts at about  $147^\circ$  and is sparingly soluble in dry ether, chloroform, light petroleum, or benzene, but readily so in hot water or methyl alcohol.

*The Semicarbazone of  $\delta$ -Keto-hexahydrobenzoic acid*,

$\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{N}:\text{C}(\text{CH}_2\cdot\text{CH}_2)_2\text{CH}\cdot\text{CO}_2\text{H}$ .

When keto-hexahydrobenzoic acid is dissolved in a little water and mixed with a solution of semicarbazide hydrochloride and sodium

acetate, the semicarbazone separates at once as a sandy, crystalline powder.

0.1605 gave 28.7 c.c. nitrogen at  $17^\circ$  and 761 mm.  $N = 20.8$ .

$C_9H_{13}O_3N_3$  requires  $N = 21.2$  per cent.

This semicarbazone softens at about  $194^\circ$  and decomposes at  $200^\circ$ ; it is very sparingly soluble in water and in alcohol. It dissolves readily in hydrochloric acid with liberation of the keto-acid, which may then be extracted with ether (see p. 425).

*Action of Phenylhydrazine on  $\delta$ -Keto-hexahydrobenzoic Acid. Formation of Tetrahydrocarbazole-p-carboxylic Acid.\**

A solution of the pure keto-acid (1 gram) in water was mixed with freshly distilled phenylhydrazine (2 grams) dissolved in dilute acetic acid, when, in a short time, pale yellow drops separated which, doubtless, consisted of hydrazone of the keto-acid. The substance showed, however, no signs of crystallising, and therefore no attempts were made to analyse it; it is also evidently an unstable substance, since it rapidly became brown and gave off gas. The freshly prepared oily hydrazone dissolves in warm concentrated hydrochloric acid, and, if the solution is heated just to boiling and then poured into cold water, an ochre-coloured precipitate of crude tetrahydrocarbazolecarboxylic acid separates.

The precipitate was collected at the pump, washed well with water, and left in contact with porous porcelain until quite dry; it was then digested with benzene, filtered from a brown, amorphous impurity, and the benzene solution evaporated to a small bulk.

The concentrated solution gradually deposited a crust of warty crystals which was collected, washed with benzene, dried at  $100^\circ$ , and analysed.

0.1635 gave 0.4364  $CO_2$  and 0.0890  $H_2O$ .  $C = 72.8$ ;  $H = 6.0$ .

0.2184 „ 11.4 c.c. nitrogen at  $15^\circ$  and 749 mm.  $N = 6.1$ .

$C_{13}H_{13}O_2N$  requires  $C = 72.6$ ;  $H = 6.0$ ;  $N = 6.5$  per cent.

*Tetrahydrocarbazole-p-carboxylic acid* melts at about  $195^\circ$  and is readily soluble in alcohol, but sparingly so in chloroform, light petroleum, or benzene. The solution in sodium carbonate decolorises permanganate instantaneously. The finely powdered substance dissolves readily in concentrated hydrochloric acid and is reprecipitated in flocks on dilution with water. When the acid is heated in a test-tube, it gives off gas and yields a crystalline sublimate which is only partially soluble in sodium carbonate and has a pronounced odour of indole.

\* For the constitution of this acid, see p. 419.

*Carboxyhexamethenyl- $\delta$ -keto-hexahydrobenzoic Acid.*

As explained in the introduction (p. 419), the ester of this acid was accidentally obtained in the course of an experiment made with the object of preparing methyl  $\delta$ -keto-hexahydrobenzoate from the acid by treatment with methyl alcohol and sulphuric acid in the usual way; the details of the experiment are as follows.

The acid (70 grams) was dissolved in methyl alcohol (200 c.c.), and concentrated sulphuric acid (50 c.c.) gradually added, the whole being well cooled during the addition. The mixture was digested for 4 hours in a reflux apparatus, and, when cold, mixed with 3 volumes of ether; water was then added and the ethereal solution separated and washed successively with water and dilute sodium carbonate. After drying over calcium chloride and evaporating, a viscid oil remained which, on fractionating under 20 mm. pressure, was readily separated into methyl  $\delta$ -keto-hexahydrobenzoate boiling at  $140^{\circ}$  (see p. 426) and a yellow, viscid liquid boiling at  $255^{\circ}$ . The latter was analysed with the following results:

0.266 gave 0.6356  $\text{CO}_2$  and 0.178  $\text{H}_2\text{O}$ .  $\text{C} = 65.2$ ;  $\text{H} = 7.4$ .

$\text{C}_{16}\text{H}_{22}\text{O}_5$  requires  $\text{C} = 65.3$ ;  $\text{H} = 7.5$  per cent.

In order to obtain the free acid, this *methyl carboxyhexamethenyl- $\delta$ -keto-hexahydrobenzoate* was dissolved in methyl alcohol mixed with a methyl alcoholic solution of caustic potash (8 grams) and heated to boiling for half an hour. Water was then added and the solution evaporated until free from methyl alcohol; it was then acidified, when a viscid syrup separated which gradually solidified.

After remaining in contact with porous porcelain until quite free from oily impurity, the acid was dissolved in dry ether, the ethereal solution concentrated and allowed to remain, when the acid gradually separated as a hard, crystalline crust.

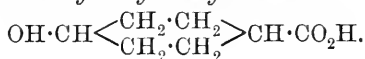
0.1508 gave 0.3474  $\text{CO}_2$  and 0.0958  $\text{H}_2\text{O}$ .  $\text{C} = 62.8$ ;  $\text{H} = 7.0$ .

$\text{C}_{14}\text{H}_{18}\text{O}_5$  requires  $\text{C} = 63.1$ ;  $\text{H} = 6.8$  per cent.

*Carboxyhexamethenyl- $\delta$ -keto-hexahydrobenzoic acid* melts at about  $170^{\circ}$ , but not sharply, since it softens a good deal below that temperature.

It is readily soluble in alcohol, but sparingly so in ether and cold water; it dissolves, however, in hot water, and separates on cooling, in colourless, microscopic needles. The solution in dilute sodium carbonate instantly decolorises permanganate, and when the aqueous solution of the acid is boiled with semicarbazide hydrochloride and sodium acetate, a very sparingly soluble semicarbazone is formed which was not further examined.

*Reduction of  $\delta$ -Keto-hexahydrobenzoic Acid. Formation of  
trans- $\delta$ -Hydroxyhexahydrobenzoic Acid,*



Sodium amalgam readily reduces  $\delta$ -keto-hexahydrobenzoic acid to the above hydroxy-acid, and, in studying this reduction, the keto-acid, in quantities of 5 grams, was dissolved in a slight excess of dilute sodium carbonate solution and treated with 150 grams of 4 per cent. sodium amalgam. The reduction was carried out in a large porcelain beaker, fitted with a mechanical stirrer and cooled externally by ice, and the sodium amalgam was added in quantities of 30 grams, a stream of carbon dioxide being passed during the whole operation. The product from 5 of these operations was separated from the mercury, acidified and extracted 10 times with ether, and since, even then, 8 grams of the reduced acid remained in the mother liquor, the extraction was continued by shaking on the machine with large quantities of ether. The combined ethereal extracts were dried over calcium chloride and evaporated to a small bulk, when the hydroxy-acid (15 grams) gradually separated in colourless nodules, and was further purified by a second recrystallisation from ether.

0.1860 gave 0.3982  $\text{CO}_2$  and 0.1391  $\text{H}_2\text{O}$ . C = 58.4; H = 8.3.

0.1676 „ 0.3574  $\text{CO}_2$  „ 0.1254  $\text{H}_2\text{O}$ . C = 58.2; H = 8.3.

$\text{C}_7\text{H}_{12}\text{O}_3$  requires C = 58.3; H = 8.3 per cent.

*trans- $\delta$ -Hydroxyhexahydrobenzoic acid* melts at 120—121°, and is readily soluble in water or alcohol, but sparingly so in cold dry ether, chloroform, or benzene. This acid shows no tendency to yield a lactone; when heated, it distils, and the oily distillate, which solidifies on rubbing, is completely soluble in cold sodium carbonate solution, and when the acid is boiled with 25 per cent. sulphuric acid, no signs of lactone formation could be detected.

The ethereal mother liquors of the *trans*-hydroxy-acid were evaporated to dryness and left for some days until the whole had become semi-solid. The mass was then spread on porous porcelain, and, when quite free from oil, recrystallised from ether, and in this way 5 grams of the pure *trans*-hydroxy-acid were obtained.

In order to see whether any *cis*-hydroxy-acid had been formed during the reduction of the keto-acid, the porous porcelain was broken up and extracted in a Soxhlet apparatus with ether, but only a small quantity of oil was obtained, and after distilling this under 30 mm. pressure the distillate was found to be completely soluble

in cold dilute sodium carbonate solution, showing that no trace of lactone was present, and thus proving that no *cis*-hydroxy-acid had been formed.

*trans*- $\delta$ -Bromohexahydrobenzoic Acid and its Conversion into  $\Delta^3$ -Tetrahydrobenzoic Acid,



and into  $\gamma$ -Bromohexahydrobenzoic Acid and  $\gamma\delta$ -Dibromohexahydrobenzoic Acid.

When finely-powdered  $\delta$ -hydroxyhexahydrobenzoic acid is mixed with hydrobromic acid (saturated at  $0^\circ$ ), it dissolves, and even after several hours no separation takes place.

If, however, the solution is heated in a sealed tube at  $100^\circ$  for 30 minutes, a viscid, oily layer forms on the surface of the hydrobromic acid, and this gradually becomes semi-solid. After washing with water, contact with porous porcelain readily removes the oily impurity, and the residue crystallises readily from light petroleum (b. p.  $70$ — $80^\circ$ ) in colourless, glistening plates.

0.1388 gave 0.1254 AgBr. Br = 38.4.

$\text{C}_7\text{H}_{11}\text{O}_2\text{Br}$  requires Br = 38.6 per cent.

*trans*- $\delta$ -Bromohexahydrobenzoic acid softens at  $160^\circ$  and melts at about  $167^\circ$ , and is readily soluble in chloroform, benzene, or alcohol, but less so in cold light petroleum.

When the bromo-acid is boiled with water, hydrogen bromide is only slowly eliminated, and, indeed, the acid crystallises well from water if the operation is carried out moderately rapidly, and is then obtained in plates having a satiny lustre and exactly resembling benzoic acid, and, like this acid, the bromo-acid is also volatile in steam.

$\Delta^3$ -Tetrahydrobenzoic Acid.—In preparing this acid,  $\delta$ -bromohexahydrobenzoic acid was dissolved in a considerable excess of moderately concentrated sodium carbonate and the solution heated to boiling for half an hour. On acidifying,  $\Delta^3$ -tetrahydrobenzoic acid was precipitated as a colourless oil, and, after extracting [with ether, the ethereal solution was dried over calcium chloride, evaporated, and the residue distilled under 25 mm. pressure.

With the exception of a small quantity of a higher boiling substance (probably  $\delta$ -hydroxyhexahydrobenzoic acid, produced from the bromo-acid by hydrolysis), the whole passed over at  $145$ — $150^\circ$ , and, on

subsequently distilling under the ordinary pressure, the acid was readily obtained pure as a colourless oil boiling constantly at  $237^{\circ}$  (748 mm.).

0.2348 gave 0.5700  $\text{CO}_2$  and 0.1686  $\text{H}_2\text{O}$ .  $\text{C} = 66.2$ ;  $\text{H} = 8.0$ .

0.1490 „ 0.3626  $\text{CO}_2$  „ 0.1064  $\text{H}_2\text{O}$ .  $\text{C} = 66.4$ ;  $\text{H} = 7.9$ .

$\text{C}_7\text{H}_{10}\text{O}_2$  requires  $\text{C} = 66.6$ ;  $\text{H} = 7.9$  per cent.

When placed in a freezing mixture, the distilled acid solidified completely, and the melting point, determined by placing a thermometer in the melting acid, was about  $13^{\circ}$ . Possibly, if the acid were left in contact with porous porcelain in order to remove any trace of oily impurity, a higher melting point than this might be observed, but the amount of material at my disposal did not allow of this being done.  $\Delta^3$ -Tetrahydrobenzoic acid has a most unpleasant odour, closely resembling that of allylacetic acid; it shows the properties of an unsaturated acid, since its solution in sodium carbonate decolorises permanganate instantly and the acid itself combines directly with both bromine and hydrogen bromide (see below). When the acid is exposed on a watch glass to the action of the air, very little change is noticed until after some days, and then a thin film of crystals forms on the surface, and these crystals appear to consist of benzoic acid, although this could not be established with certainty.

In any case, oxidation takes place only very slowly, and in this respect the  $\Delta^3$ -acid resembles the  $\Delta^1$ -acid and differs from the  $\Delta^2$ -acid, as the latter is rapidly oxidised to benzoic acid in contact with air.  $\Delta^3$ -Tetrahydrobenzoic acid shows no signs of being converted into a lactone when it is digested with dilute sulphuric acid.

*$\gamma$ -Bromohexahydrobenzoic Acid.*— $\Delta^3$ -Tetrahydrobenzoic acid dissolves readily and completely in four times its volume of aqueous hydrobromic acid (saturated at  $0^{\circ}$ ) with evolution of heat, but the solution soon becomes cloudy, and in a short time a viscid oil separates on the surface of the hydrobromic acid. The oil gradually solidifies, and the aqueous layer becomes filled with colourless crystals.

After 12 hours, water is added, the pasty, crystalline mass collected at the pump, washed well, and left in contact with porous porcelain until quite dry. The residue crystallises from its warm dilute solution in light petroleum (b. p.  $60$ – $80^{\circ}$ ) in groups of flat needles, but from a hot concentrated solution the substance separates in glistening plates.

0.1712 gave 0.1552 AgBr.  $\text{Br} = 38.6$ .

$\text{C}_7\text{H}_{11}\text{O}_2\text{Br}$  requires  $\text{Br} = 38.6$  per cent.

*$\gamma$ -Bromohexahydrobenzoic acid* shrinks together at  $110^{\circ}$  and melts at about  $122^{\circ}$ , and repeated crystallisation did not alter this behaviour or make the melting point any sharper; it is practically insoluble in cold

light petroleum or cold water, but readily soluble in benzene, alcohol, or ether. It dissolves to a considerable extent in boiling water, and separates, on cooling, as a voluminous mass of glistening plates which closely resemble benzoic acid.

In its behaviour towards sodium carbonate, this  $\gamma$ -bromo-acid differs in a marked manner from the  $\delta$ -bromo-acid (see above), since, after boiling for half an hour and acidifying, no sparingly soluble tetrahydrobenzoic acid separates. On extracting with ether, a very soluble oily acid is obtained, which rapidly becomes insoluble in sodium carbonate and develops the odour of a lactone. It is probable that the neutral oil produced in this way is the lactone of  $\gamma$ -hydroxyhexahydrobenzoic acid.

*$\gamma\delta$ -Dibromohexahydrobenzoic Acid.*—When the solution of tetrahydrobenzoic acid in chloroform is cooled to  $-10^\circ$  and treated with bromine, the colour of the halogen disappears instantly, and only traces of hydrogen bromide are formed. As soon as the solution had acquired a permanent pale yellow tint, it was transferred to a large watch glass and left until the chloroform had evaporated. A viscid, colourless oil resulted which did not crystallise for some days, but ultimately solidified almost completely. The mass was rapidly washed with formic acid (sp. gr. 1.22) and recrystallised from this solvent, from which the dibromo-acid separates in small, glistening crystals.

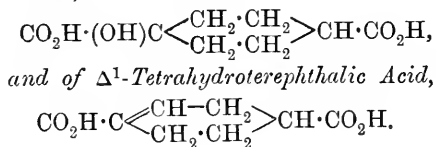
0.1444 gave 0.1888 AgBr. Br = 55.6.

$C_7H_{10}O_2Br_2$  requires Br = 55.9 per cent.

*$\gamma\delta$ -Dibromohexahydrobenzoic acid* melts at  $84-86^\circ$ , and is sparingly soluble in cold formic acid and light petroleum, but readily so in alcohol, ether, or chloroform. It dissolves readily in sodium carbonate, and, if the solution is boiled for 5 minutes and then acidified, nothing separates, but ether extracts a very readily soluble syrupy acid which, when kept, shows signs of crystallising.

Since this acid reduces ammoniacal silver solution, but does not decolorise permanganate, it is probably  $\gamma\delta$ -dihydroxyhexahydrobenzoic acid produced from the dibromo-acid by hydrolysis.

*Action of Hydrogen Cyanide on  $\delta$ -Keto-hexahydrobenzoic Acid. Formation of the cis- and trans-Modifications of  $\alpha$ -Hydroxyhexahydro-terephthalic Acid,*



In the first experiments on the action of hydrogen cyanide on  $\delta$ -keto-hexahydrobenzoic acid, the conditions recommended by Baeyer and Tutein (*Ber.*, 1889, 22, 2186) in the similar case of  $\gamma$ -keto-hexahydrobenzoic acid were employed, that is to say, the acid was mixed with potassium cyanide and the mixture treated with hydrochloric acid. The addition did not take place satisfactorily under these conditions, and, after several experiments, the following process, based on the observations of Lapworth (*Trans.*, 1903, 83, 995), was employed with excellent results. The pure acid (4 grams) was dissolved in a little warm water, cooled until crystallisation just commenced, and then mixed with pure potassium cyanide (5 grams) and 10 c.c. of a 15 per cent. solution of hydrocyanic acid. The liquid gradually darkened, and after 24 hours had become nearly black; it was mixed with a little hydrochloric acid and extracted 6 times with ether. After drying over calcium chloride and evaporating, a light brown syrup (5 grams) was obtained, which, on rubbing with a glass rod, rapidly became semi-solid. The mass was left in contact with porous porcelain until quite dry; the residue was dissolved in ether, the solution digested with animal charcoal, filtered, and concentrated. An equal volume of chloroform was then added and the ether distilled off, when a sandy, crystalline precipitate was soon deposited, which melted at  $180^\circ$ , and was easily identified as aminomalononitrile,  $\text{NH}_2 \cdot \text{CH}(\text{CN})_2$ , produced by the polymerisation of some of the hydrogen cyanide employed. The filtrate from this substance deposited, on spontaneous evaporation, a mass of crystals, which were collected and purified by re-dissolving in ether, adding chloroform, and distilling off the ether as before.

The glistening, pale yellow plates thus obtained consist of the nitrile of *trans- $\alpha$ -hydroxyhexahydroterephthalic acid*.

0.1805 gave 12.6 c.c. nitrogen at  $14^\circ$  and 774 mm.  $\text{N} = 8.4$ .

$\text{C}_8\text{H}_{11}\text{O}_3\text{N}$  requires  $\text{N} = 8.3$  per cent.

The melting point of this nitrile is not sharp; it begins to shrink together at  $125^\circ$  and is completely melted at  $140^\circ$ . It is readily

soluble in water or methyl alcohol, but sparingly so in chloroform, benzene, or light petroleum. When heated in a test-tube, water is eliminated and an oil distils which does not solidify on cooling, and, since the solution of this oil in sodium carbonate does not decolorise permanganate, it may very probably be the corresponding cyano-lactone. When the nitrile is hydrolysed under the conditions stated below, it yields *trans*- $\alpha$ -hydroxyhexahydroterephthalic acid.

The chloroform mother liquors of this *trans*-nitrile contain the *cis*-modification, but, as this did not appear to crystallise readily, no attempt was made to isolate it in a condition suitable for analysis.

In preparing the *cis*- and *trans*-modifications of hydroxyhexahydroterephthalic acid in quantity, 20 grams of ketohexahydrobenzoic acid were converted into the mixed nitriles, and after extracting with ether, the oil was dissolved in 100 c.c. of concentrated hydrochloric acid and heated, first on the water-bath for three hours and then to boiling for one hour. The whole was evaporated to dryness, the crystalline cake was then ground up and digested with absolute alcohol, and after filtering from the ammonium chloride the alcoholic solution was evaporated almost to dryness. The residue, which still contained ammonium chloride, was dissolved in excess of dilute barium hydroxide and boiled until the evolution of ammonia had completely ceased, the barium was then exactly removed by sulphuric acid, and the filtrate from the barium sulphate evaporated almost to dryness.

After remaining for 24 hours, the crystalline crust was left in contact with porous porcelain until quite dry, dissolved in water, digested with animal charcoal, and evaporated considerably, when a mass of white, nodular crystals of the *trans*-hydroxy-acid gradually separated. These were collected and purified by crystallising twice from water, when the substance was obtained in hard crystals containing one molecule of water of crystallisation.

After being exposed to the air for 6 days, the following results were obtained on analysis:

0.1654 gave 0.2822  $\text{CO}_2$  and 0.1023  $\text{H}_2\text{O}$ .  $\text{C} = 46.5$ ;  $\text{H} = 6.9$ .

$\text{C}_8\text{H}_{12}\text{O}_5 \cdot \text{H}_2\text{O}$  requires  $\text{C} = 46.6$ ;  $\text{H} = 6.8$  per cent.

0.2416 gram, heated at  $90^\circ$  until constant, lost 0.0221 gram or 9.1 per cent., whereas  $\text{C}_8\text{H}_{12}\text{O}_5 \cdot \text{H}_2\text{O}$  contains 8.8 per cent. of water. The anhydrous acid was also analysed.

0.1852 gave 0.3488  $\text{CO}_2$  and 0.1064  $\text{H}_2\text{O}$ .  $\text{C} = 51.3$ ;  $\text{H} = 6.4$ .

$\text{C}_8\text{H}_{12}\text{O}_5$  requires  $\text{C} = 51.1$ ;  $\text{H} = 6.4$  per cent.

On titration with decinormal caustic soda, 0.0956 gram required for

neutralisation 0.0408 NaOH, whereas this amount of a dibasic acid,  $C_8H_{12}O_5$ , should neutralise 0.0407 NaOH.

*trans- $\alpha$ -Hydroxyhexahydroterephthalic acid* melts at 228—230° with decomposition, and when heated in small quantities in a test-tube, water is eliminated and a crystalline sublimate of  $\Delta^1$ -tetrahydroterephthalic acid is obtained (p. 437). It is readily soluble in water or alcohol, but sparingly so in cold ether, chloroform, benzene, or concentrated hydrochloric acid. The neutral solution of the ammonium salt gives no precipitate with barium or calcium chloride, but a heavy caseous precipitate with lead acetate; with copper sulphate, a turbidity is produced, and, on warming, a pale blue, amorphous precipitate separates.

*cis- $\alpha$ -Hydroxyhexahydroterephthalic Acid*.—The aqueous mother liquors of the *trans*-acid yielded, on further concentration, first an additional small crop of the same acid, and afterwards the *cis*-hydroxy-acid separated in masses of irregularly shaped crystals. These were collected and purified by repeated crystallisation from water, the substance being dried at 100° before analysis.

0.1594 gave 0.2958  $CO_2$  and 0.0912  $H_2O$ .  $C=50.6$ ;  $H=6.4$ .

The substance was then recrystallised from ether and again analysed.

0.1832 gave 0.3428  $CO_2$  and 0.1052  $H_2O$ .  $C=51.0$ ;  $H=6.4$ .

$C_8H_{12}O_5$  requires  $C=51.1$ ;  $H=6.4$  per cent.

On titration, 0.1220 gram neutralised 0.051 gram NaOH, whereas this amount of a dibasic acid,  $C_8H_{12}O_5$ , should neutralise 0.052 NaOH.

*cis- $\alpha$ -Hydroxyhexahydroterephthalic acid* melts at 168—170°, and is readily soluble in water and alcohol, but sparingly so in chloroform, benzene, or ether. If, however, the finely-powdered substance is digested in a reflux apparatus with a large quantity of ether, it dissolves, and, after concentrating considerably, the pure acid gradually separates in hard, crystalline crusts. When crystallised from water, the hard nodules obtained do not, like the *trans*-acid, contain water of crystallisation, since the air-dried substance loses only very slightly in weight on drying at 90°.

If a small quantity of the dry acid is heated in a test-tube, it first melts and then gives off water, and a sublimate of  $\Delta^1$ -tetrahydroterephthalic acid forms on the cooler portions of the tube.

When the *cis*-hydroxy-acid is mixed with concentrated sulphuric acid and warmed to about 60°, carbon monoxide is evolved in quantity, and if, when the evolution has ceased, the pale yellow liquid is poured into water, a white, crystalline precipitate separates.

This was collected and found to consist of pure  $\Delta^1$ -tetrahydro-

terephthalic acid, and from the filtrate a quantity of  $\delta$ -keto-hexahydrobenzoic acid was obtained by extraction with ether and identified by conversion into the semicarbazone.

The *cis*-hydroxy-acid shows a curious behaviour when heated with fuming hydrobromic acid (saturated at  $0^\circ$ ) in a sealed tube in a boiling water-bath. The acid dissolves, and then a gas (presumably carbon dioxide) is slowly given off and, on diluting the yellow solution with water, a quantity of a very voluminous, white, amorphous precipitate separates. This substance, which contains bromine, seems to be formed quantitatively; it is practically insoluble in water, but dissolves in sodium carbonate. It separates from dilute formic acid apparently as a microcrystalline precipitate; this shrinks together at  $160$ — $165^\circ$  and has no definite melting point. This substance was not further investigated, but it was noticed that the *trans*-hydroxy-acid also appeared to show the same behaviour on heating with hydrobromic acid.

The amount of the mixed hydroxyhexahydroterephthalic acids obtained by the addition of hydrogen cyanide to  $\delta$ -keto-hexahydrobenzoic acid and subsequent hydrolysis was upwards of 70 per cent. of the theoretical, and it is interesting to note that in this way a very much larger amount of the *cis* acid is produced than of the *trans*-acid.

$\Delta^1$ -Tetrahydroterephthalic Acid.—As explained above, this acid is produced when either the *cis*- or *trans*-modification of  $\alpha$ -hydroxyhexahydroterephthalic acid is heated. In investigating this decomposition, 5 grams of the pure *cis*-acid was distilled under 10 mm. pressure, the sublimate was dissolved in hot sodium carbonate, the solution decolorised with animal charcoal, concentrated, and acidified, when the tetrahydro-acid separated as a microcrystalline deposit.

This was collected and recrystallised from much water.

0.1406 gave 0.2894  $\text{CO}_2$  and 0.0764  $\text{H}_2\text{O}$ .  $\text{C}=56.2$ ;  $\text{H}=6.0$ .

$\text{C}_8\text{H}_{10}\text{O}_4$  requires  $\text{C}=56.4$ ;  $\text{H}=5.9$  per cent.

This acid melted above  $300^\circ$  and reduced permanganate, and was evidently identical with the  $\Delta^1$ -tetrahydroterephthalic acid described by Baeyer (*Annalen*, 1888, 245, 160). In order that there should be no doubt as to its identity, the acid was converted into its methyl ester by digesting with a five per cent. solution of hydrogen chloride in methyl alcohol. The methyl ester, thus obtained, crystallised from dilute methyl alcohol in needles and melted at  $38$ — $39^\circ$ , whereas Baeyer gives  $39^\circ$  as the melting point of methyl  $\Delta^1$ -tetrahydroterephthalate.

The author wishes to express his thanks to Mr. S. S. Pickles, B.Sc.,

for valuable assistance in carrying out these experiments, and to state that much of the heavy expense entailed has been met by a grant from the Government Grant Committee of the Royal Society.

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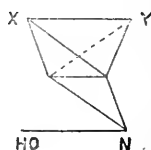
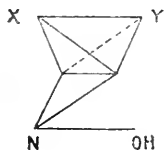
## XLIX.—*The Arrangement in Space of the Groups Combined with the Tervalent Nitrogen Atom.*

By FREDERIC STANLEY KIPPING and ARTHUR HENRY SALWAY.

THE discussion as to the cause of the existence of isomeric oximes and of that of certain other derivatives of tervalent nitrogen, which for so many years occupied a prominent place in current chemical literature, apparently came to an end some time ago; at any rate, the occurrence of such isomerides now excites but little interest, and is, in fact, taken as a matter of course, and the usual "*syn*" and "*anti*" configurations having been respectively assigned to the two isomerides, the matter is dismissed from further consideration.

It is far from our intention to attempt to make any review of the literature of this subject, as it would occupy far too much space even were we merely to refer in the briefest manner to the views of the principal workers in this field, or to recapitulate quite cursorily the various arguments which have led to the adoption of the "*syn*" and "*anti*" configurational formulæ for isomeric derivatives of tervalent nitrogen; it is necessary, however, in order to explain one of the objects of this investigation, to briefly recall the meaning and consequences of such stereochemical representations.

According to Hantzsch and Werner (*Ber.*, 1890, 23, 11), the existence of this type of isomerides is to be explained by assuming that the groups around a tervalent nitrogen atom are situated at the corners of a regular tetrahedron, of which the nitrogen atom itself occupies the fourth corner; the "*syn*" and "*anti*" configurations are thus respectively represented by the following symbols:



Now this hypothesis, which seems to be generally accepted by chemists as a means of explaining the phenomenon in question, involves, or seems to involve, certain consequences which are by no means confirmed by experimental evidence.

In the first place, this conception premises the existence of isomerides in the case of a great number of compounds which hitherto have been obtained in only one form (compare Hantzsch and Werner, *loc. cit.*). Azobenzene, for example, as far as is known, does not exhibit stereoisomerism, and yet the existence of *syn*- and *anti*-forms of this and of azo- and azoxy-compounds generally would be in accordance with theory; as a matter of fact, the only cases of isomerism in such compounds which have yet been described are those of *p*-azoxy-toluene and trinitrazotoluene (Janovski and Reimann, *Ber.*, 1889, 22, 40, and Janovski, *Ber.*, 1889, 22, 1172), and it would appear that even these may be capable of some other explanation. Many other examples of a similar absence of conceivable isomerides might be quoted, but it is unnecessary to do so; Hantzsch, himself, has tried to obtain isomeric compounds containing doubly-linked nitrogen in many cases where their existence seemed a probable consequence of his and Werner's theory (compare *Ber.*, 1893, 26, 926).

The question which more immediately concerns our work, however, is that of the possibility of existence of isomerism in compounds of the type  $\text{NR}_1\text{R}_2\text{R}_3$ ; if the three atoms or groups combined with trivalent nitrogen are situated at the angles of a regular tetrahedron, secondary and tertiary nitrogen bases which are of the above type, that is to say, in which the three atoms or groups are all different from one another, should exist in enantiomorphously related forms, and the latter in all probability would be optically active; such forms would be represented respectively by the configurational formulæ:

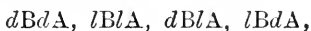


The possibility of the existence of such isomerides has been previously considered, and, in fact, experiments have already been made in order to try and obtain such optically active compounds. Kraft (*Ber.*, 1890, 23, 2780), at the suggestion of Hantzsch, attempted to resolve benzylethylamine and *p*-tolylhydrazine by fractionally crystallising their hydrogen tartrates, whereas Behrend and König (*Annalen*, 1891, 263, 175; *Ber.*, 1891, 24, 447c) carried out similar and additional

experiments with  $\beta$ -benzylhydroxylamine, whilst Ladenburg (*Ber.*, 1893, 26, 864) investigated methylaniline, tetrahydroquinoline, and tetrahydropyridine; all these investigations, and likewise some experiments of Le Bel (*Compt. rend.*, 1891, 112, 11), were, however, uniformly unsuccessful.

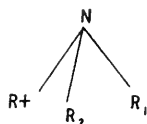
Now it may be observed in connection with the investigations just referred to that the point actually put to the test of experiment was not so much the existence of isomeric tervalent as that of quinquevalent derivatives of nitrogen containing two identical groups or atoms. Even had isomeric salts been obtained, the latter might not have afforded enantiomorphously related bases when decomposed with alkalis, because in passing from the quinquevalent to the tervalent state a complete rearrangement in space of the nitrogen "valencies" might occur, and both the isomeric salts might give the same compound or the same mixture of isomerides.

These considerations led us to undertake the present work in the hope of adding to our knowledge of the configuration of tervalent nitrogen. Our first experiments were directed towards an investigation of the products obtained by the action of an externally compensated acid chloride on certain primary and secondary amines. A *dl*-acid chloride, such as *dl*-phenylchloroacetyl chloride, gives with a *dl*-base, such as *dl*-hydrindamine, a mixture of two isomeric phenylchloroacetohydrindamides, which can be separated by fractional crystallisation (Kipping and Hall, *Trans.*, 1901, 79, 444); this is due, of course, to the formation of the four compounds,



which are enantiomorphously related in pairs, and which crystallise together, forming two different *dl*-isomerides. An externally compensated acid chloride may therefore be employed for the detection of asymmetry in bases, a fact which in the first place we confirmed by proving that *dl*-benzylmethylacetyl chloride gives with *dl*-hydrindamine a mixture of isomeric *dl*-substituted amides from which the two compounds may be isolated without much difficulty.

Now if instead of a base such as *dl*-hydrindamine, which owes its asymmetry to a carbon group, some primary or secondary base, such as *p*-toluidine or methylaniline, were treated with a *dl*-acid chloride, it seems reasonable to suppose that two isomeric substituted amides should be obtained, provided that the three nitrogen valencies are not arranged in one plane, but, as surmised by Hantzsch and Werner in the case of the oximes; the *d*-component of the acid chloride would give equal or approximately equal quantities of the two compounds,



which are not enantiomorphously related, whilst the *l*-component would give rise to two analogous isomerides; these would then crystallise in pairs, just as in the case of the hydrindamides, giving two different *dl*-substituted amides.

The experiments were tried with methylaniline, *p*-toluidine, phenylhydrazine, and benzylaniline, the acid chloride being *dl*-benzylmethylacetyl chloride; in no case, however, could we observe the least indication of the formation of isomerides.

In all these examples, if non-enantiomorphously related isomerides were produced at all, each of the four compounds which might conceivably have been formed would contain one group enantiomorphously related to that in one of its isomerides; thus, although *dBdA* and *dBIA* are not enantiomorphously related, a portion of the molecule of the one does bear such a relationship to a portion of that of the other; similarly with *lBIA* and *lBdA*. This might condition the formation of a double racemic salt  $\left\{ \begin{array}{l} \textit{dBdA}, \textit{dBIA} \\ \textit{lBIA}, \textit{lBdA} \end{array} \right\}$  such as is possibly produced from *dl*-hydrindamine and *dl*-mandelic acid (Kipping and Hall, *Trans.*, 1901, 79, 442), and thus account for the failure of our attempts to separate isomerides.

In order to limit such a possibility to some extent, we next made experiments on the behaviour of some primary and secondary bases towards optically active benzylmethylacetyl chloride, and examined the substituted amides derived from *p*-toluidine and benzylaniline; no evidence of the formation of isomerides *dBdA* and *lBdA*, however, could be obtained.

Our last and most conclusive experiments on these lines were made with optically active bases and optically active benzylmethylacetyl chloride. If, in the case of asymmetric carbon groups, the two enantiomorphously related compounds are generally separable as soon as an asymmetric radicle is substituted for one of the atoms or radicles in each of the groups, it would seem highly probable that the introduction of a second centre of asymmetry would greatly enhance the difference between the two isomerides as regards their solubility, &c., and thus greatly facilitate their separation by fractional crystallisation.

Now when an optically active base such as *l*-menthylamine is treated with *d*-benzylmethylacetyl chloride, the resulting substituted amide contains two centres of asymmetry due to carbon; if, in addition,

the three nitrogen valencies are so arranged as to condition a third centre of asymmetry, two very different isomerides, represented respectively by the following configurational formulæ, should be obtained:

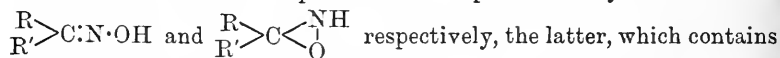


The bases examined in this way were *d*-hydrindamine, *l*-methylhydrindamine, *l*-menthylamine, and *l*-phenylethylamine; in all cases, however, the product seemed to consist of one substance only, and when crystallised fractionally from various solvents retained its uniform character.

We conclude from these results that the three radicles, together with the tervalent nitrogen atom itself, are situated in one plane; that two of the radicles are symmetrically grouped with respect to the third, and that in all probability this is true of any two, that is to say, the whole arrangement is the most symmetrically possible one.

*Examination of Oximes.*—Having failed to detect any indication of isomerism in the case of saturated tervalent nitrogen compounds which would be in accordance with the theory of Hantzsch and Werner, we next turned our attention to the oximes themselves.

Assuming that the isomerism of the *syn*- and *anti*-forms is structural and that the two compounds are represented by the formulæ



an asymmetric carbon group, would exist in enantiomorphously related forms. If, then, an optically active acyl group were substituted for the hydrogen atom, two non-enantiomorphously related optically active isomerides should be obtained, whereas by employing a *dl*-acyl chloride two different *dl*-compounds should be produced.

Intending, subsequently, to investigate the benzaldoximes, we first studied the action of the *dl*-acid chloride on benzoinoxime, a substance which crystallises well, and the derivatives of which, it was thought, would show a similar behaviour. The reaction, however, proceeded in a manner altogether abnormal; instead of obtaining an acyl derivative by the simple displacement of the oximic hydrogen atom, we got a number of other products, namely, benzil, benzoin, benzaldehyde, benzonitrile, ammonium chloride, hydrogen chloride, benzylmethylacetic acid, and a compound melting at 126°; this decomposition of the oxime made it impossible, of course, to accomplish the objects in view, but the result is not without interest as showing how easily the

benzoin molecule—which is generally so stable—may undergo decomposition.

In order to try and throw some light on this extraordinary reaction, we next studied the action of benzoyl chloride on benzoinoxime, but found that interaction proceeded in a normal manner, giving a benzoinoxime benzoate in which the benzoyl group had displaced the oximic hydrogen atom; the constitution of the product was established by preparing the oxime of the benzoylbenzoin described by Zinin (*Annalen*, 1857, 104, 117); the latter, which would necessarily have the constitution  $C_6H_5 \cdot CH(Obz) \cdot CPh : N \cdot OH$ , is not identical with the benzoyl derivative of benzoinoxime, so that our compound must be represented by the formula  $C_6H_5 \cdot CH(OH) \cdot CPh : N \cdot Obz$ .

Failing to obtain the desired results with benzoinoxime, we made a few experiments with  $\alpha$ -benzaldoxime, but were unable to prepare the benzylmethylacetyl derivative owing to the decomposition of the aldoxime into benzonitrile.

*The Resolution of dl-Bases with the aid of d-Benzylmethylacetyl Chloride.*

The resolution of a *dl*-base by fractionally crystallising the salt obtained by combining it with an optically active acid is very often unsuccessful owing to the fact that the two salts *dBdA* and *lBdA* or *dBIA* and *lBIA* may differ so slightly in solubility that no appreciable separation occurs, or, again, they may unite to form a partially racemic compound. Judging from the many cases which have been examined in this laboratory, it would seem that it is rather the exception than the rule for a resolution to take place, and were all the negative results of investigators on record, this conclusion would probably be amply substantiated; contrary to the views sometimes held, the use, in such experiments, of a relatively weak acid also seems to be just as likely to give satisfactory results as that of a relatively strong one, since hydrolytic dissociation seldom plays any important part, the difference in solubility of the salts being practically the only factor of importance.

The investigations carried out during the last few years on the behaviour of *dl*-hydrindamine have shown that the resolution of this base presents more than the usual difficulties, and that ordinary fractional crystallisation of its salts with *d*-bromocamphorsulphonic, *d*-chlorocamphorsulphonic, Reyhler's *d*-camphorsulphonic, *l*-mandelic, and *d*-tartaric acids fails to effect a separation of the two isomerides. In these circumstances, it occurred to one of us that a resolution might be accomplished by using an optically active acid chloride which would probably give isomeric substituted amides differing considerably in solubility; this expectation proved to be well-founded, inasmuch as

the product of interaction of *dl*-hydrindamine and *d*-benzylmethylacetyl chloride was easily separated into two isomerides having different specific rotations.

*d*-Benzylmethylacetyl chloride was also employed for the resolution of *dl*-phenylethylamine, and in this case also the two isomeric amides corresponding with the *d*- and *l*-bases respectively are separated without much difficulty.

Judging from these examples, an optically active acid chloride may be employed with success when the use of an acid gives unsatisfactory results, but it will be necessary to wait until a greater number of cases have been tried before concluding that such a method is universally applicable. One great drawback to the use of the acid chloride is that it may be impossible to obtain the optically active bases themselves, either because the substituted amides are so stable that they cannot be hydrolysed, or because so high a temperature is required to bring about hydrolysis that the bases undergo racemisation. Thus, in the case of the benzylmethylacetohydrindamide, all attempts to regenerate the base were unsuccessful; the amides are exceedingly stable towards ordinary hydrolysing agents at moderate temperatures, and although change occurs at high temperatures, it results in the formation of indene and ammonia.

The application of an optically active acid chloride for the resolution of *dl*-alcohols or other *dl*-hydroxy-compounds has not yet been tried.

#### EXPERIMENTAL.

##### *dl Hydrindamine and dl-Benzylmethylacetyl Chloride. Isolation of Two Isomerides.*

In order to satisfy ourselves that *dl*-benzylmethylacetyl chloride would prove serviceable in detecting asymmetry, we first tried its action on *dl*-hydrindamine, a base which is very prone to form partially racemic salts, and which is resolved into its enantiomorphously related components only with great difficulty.

On adding the *dl*-benzylmethylacetyl chloride to the *dl*-base, both in ethereal solution, a development of heat occurred, and the hydrochloride of the base separated in crystals; after filtering, washing with water, and evaporating the ethereal solution, the substituted amide was obtained as an oil which rapidly solidified.

When crystallised fractionally from methyl alcohol, ether, and other solvents, this product, which at first melts indefinitely at about 70°, is finally resolved into two isomerides. One of these crystallises in thick, transparent prisms melting at 110—111°, but when the partially melted substance is allowed to cool it immediately solidifies, and when heated again melts at about 126°; it is therefore dimorphous.

This amide is very readily soluble in cold methyl alcohol, moderately so in ether, but dissolves very sparingly in light petroleum (b. p. 40—60°).

0.1615 gave 0.4857 CO<sub>2</sub> and 0.1090 H<sub>2</sub>O. C = 82.0; H = 7.5.

C<sub>19</sub>H<sub>21</sub>ON requires C = 81.7; H = 7.5 per cent.

The second isomeride crystallised from aqueous methyl alcohol in felted masses of needles melting sharply at 119.5°; it seems to be far less soluble in cold ether than the preceding compound.

0.1497 gave 0.4484 CO<sub>2</sub> and 0.0996 H<sub>2</sub>O. C = 81.7; H = 7.4.

C<sub>19</sub>H<sub>21</sub>ON requires C = 81.7; H = 7.5 per cent.

*Products from dl-Benzylmethylacetyl Chloride and Primary or Secondary Bases.*

Having proved that evidence of asymmetry due to a carbon group is easily obtained with the aid of *dl*-benzylmethylacetyl chloride, we studied the products of the action of this compound on some primary and secondary bases.

Methylaniline and the *dl*-chloride interact readily in ethereal solution. The resulting substituted amide remained in an oily condition for a long time, but ultimately solidified completely; it was fractionally crystallised from warm light petroleum (b. p. 30—40°) in which it was readily soluble, and was thus obtained in lustrous, transparent prisms melting sharply at 54—55°; all the fractions had the same appearance, and except the last, which melted a few degrees below 54°, liquefied at the same temperature. *Benzylmethylacetomethylanilide* exists, therefore, in only one form; it is readily soluble in all ordinary organic solvents.

*p*-Toluidine and *dl*-benzylmethylacetyl chloride interact vigorously in ethereal solution; the *benzylmethylaceto-p-toluidide*, which is thus formed, solidified readily, and was fractionally crystallised from aqueous alcohol; it separated in concentrically grouped needles melting at 130°. The very last mother liquors gave traces of a product melting about 2° lower than the rest, but there was no evidence of the existence of isomerides. *Benzylmethylaceto-p-toluidide* is readily soluble in all ordinary organic solvents with the exception of light petroleum (b. p. 30—40°), in which it dissolves somewhat sparingly.

Benzylaniline and *dl*-benzylmethylacetyl chloride give a product which is at first rather difficult to obtain in a crystalline condition, but which afterwards crystallises easily from aqueous alcohol in ill-defined prisms; the compound was separated into a number of fractions, but the latter were all identical in appearance and melting point.

*Benzylmethylacetobenzylanilide* is readily soluble in most organic solvents and melts at 69—70°.

0.1452 gave 0.4457 CO<sub>2</sub> and 0.0921 H<sub>2</sub>O. C = 83.7; H = 7.05.  
 C<sub>6</sub>H<sub>5</sub>·CH<sub>2</sub>·CH(CH<sub>3</sub>)·CO·N(C<sub>7</sub>H<sub>7</sub>)·C<sub>6</sub>H<sub>5</sub> requires C = 83.9; H = 7.0 per cent.

Phenylhydrazine, when treated with the *dl*-chloride in ethereal solution, readily yielded *benzylmethylacetophenylhydrazide*, which crystallised from methyl alcohol in large, transparent, lustrous prisms melting at 116—117° and readily soluble in ethyl acetate; fractional crystallisation failed to indicate the presence of an isomeride.

*Products from d-Benzylmethylacetyl Chloride and Primary or Secondary Bases.*

For the reasons already stated, we next examined the products obtained with the aid of the optically active chloride; in doing so, it was found that even when the acid chloride had the highest specific rotation previously observed, namely,  $[\alpha]_D + 18^\circ$  in ethereal solution (Kipping and Hunter, *Trans.*, 1903, 83, 1005), it still contained a small quantity of the *l*-isomeride, owing, doubtless, to the occurrence of racemisation during its preparation, and gave rise to some of the *dl*-substituted amide; the presence of the latter was a serious disadvantage because, although the main portions of the active and inactive amides could be separated without much difficulty, there still remained a considerable quantity of mixed products in which the required isomeric active compound might conceivably be concealed. In the later and more important experiments, therefore, the active acid chloride was prepared from very carefully purified acid by a method which should exclude the possibility of racemisation (p. 447).

*p*-Toluidine and *d*-benzylmethylacetyl chloride gave a product which, when repeatedly fractionally crystallised from aqueous alcohol, was resolved into two compounds, one of which, however, was present in relatively small proportions; this was the amide of the *dl*-acid and melted at 130° (p. 445). The main component, namely, *d*-benzylmethylaceto-*p*-toluidide, crystallised in large, flat, transparent, well-defined prisms melting at 115—116°; it was readily soluble in cold alcohol and in ethyl acetate.

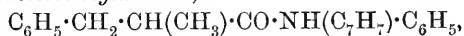
0.2364, dissolved in alcohol and the solution diluted to 25 c.c., gave, in a 200 mm. tube,  $\alpha + 3.17^\circ$ , whence  $[\alpha]_D + 167.6^\circ$ .

0.5150, dissolved in chloroform and the solution diluted to 20 c.c., gave, in a 200 mm. tube,  $\alpha + 5.67^\circ$ , whence  $[\alpha]_D + 110.1^\circ$ .

During the fractional crystallisation, no compound other than the

two already mentioned was obtained, and we concluded that optically active isomerides were not produced. The experiment was subsequently repeated, using a sample of *d*-chloride free from the *l*-isomeride, and in this case only one compound, namely, that melting at 115—116°, was obtained.

Benzylaniline and *d*-benzylmethylacetyl chloride gave a product which was very difficult to crystallise even when the acid chloride had been prepared by the special method to be described later. This was due to the fact that the product retained benzylaniline very tenaciously, and repeated washing with warm hydrochloric acid was required before the whole of this base was removed. Finally, however, the amide solidified to a crystalline mass, which was fractionally crystallised from light petroleum and from aqueous alcohol. The several fractions of *d*-benzylmethylacetobenzylanilide,



thus obtained melted at the same temperature (69—70°), which is also the melting point of the inactive amide already described (p. 446); moreover, a mixture of the crystals of the active and inactive amides also melted at 69—70°.

The specific rotation of the *d*-anilide was determined in chloroform solution: 0.3079, dissolved in chloroform, the solution diluted to 20 c.c. and examined in a 200 mm. tube, gave  $\alpha + 0.27^\circ$  whence  $[\alpha]_D + 8.8^\circ$ ; in methyl-alcoholic solution the specific rotation was  $[\alpha]_D + 16^\circ$ .

Although only one active compound was isolated, and although there was no evidence of the formation of an isomeride in the above experiment, we are unable to state positively that only one substance was produced, as a portion of the product from the last mother liquors crystallised badly and had a brown colour, doubtless owing to atmospheric oxidation.

#### *Preparation of d-Benzylmethylacetyl Chloride.*

Owing to the readiness with which the *d*-acid chloride is racemised under the influence of heat (Kipping and Hunter, *Trans.*, *loc. cit.*), the compound prepared in the usual manner is almost invariably mixed with more or less of the *l*-isomeride, the presence of which is very objectionable in such experiments as those already described, where it is a question of the existence of isomeric amides. In order to prepare the active compound in an optically pure condition, it is necessary to keep the temperature as low as possible and then to remove the phosphorus oxychloride from the product without the application of heat. This can be accomplished by passing a current of dry air through the mixture under greatly reduced pressure, but the operation requires a considerable time before the last portions of phosphorus oxychloride

are removed. The *d*-chloride thus prepared has a specific rotation in light petroleum  $[\alpha]_D + 26.2$ , a value which is a trifle higher than that previously obtained (*loc. cit.*).

This method of preparation does not remove every trace of phosphorus compounds, for the acid chloride still gives a slight reaction with ammonium molybdate, probably due to the presence of phosphoric acid; this impurity, however, is of little consequence, as it is easily eliminated by washing with water, when the acid chloride is used for the preparation of a substituted amide.

*Products from d-Benzylmethylacetyl Chloride and Optically Active Bases.*

1. *1-Phenylethylamine*.—The active base, prepared by the method recently described (Kipping and Hunter, *Trans.*, 1903, 83, 1147), was dissolved in dry ether and the active acid chloride added gradually, when a reaction immediately occurred, and the hydrochloride separated in crystals. This salt was removed by filtration, and the ethereal solution washed successively with dilute hydrochloric acid, water, sodium carbonate, and water, by which treatment any remaining hydrochloride, free base, or free acid is removed. After evaporating off the ether, the crude product, which immediately solidified, was then fractionally crystallised from benzene and thus separated into at least nine fractions, but one and the same compound melting at  $122^\circ$  was obtained throughout, and no indication whatever of the presence of isomerides was observed. *d-Benzylmethylaceto-1-phenylethylamide*,  $C_6H_5 \cdot CH_2 \cdot CH(CH_3) \cdot CO \cdot NH \cdot CH(CH_3) \cdot C_6H_5$ , crystallises from benzene in beautiful, long, silky needles melting at  $122.5^\circ$ . It is readily soluble in ethyl acetate, chloroform, methyl alcohol, ether, or alcohol, but only sparingly so in light petroleum.

0.4315, dissolved in ether and diluted to 20 c.c., gave, in a 200 mm. tube,  $\alpha + 0.37^\circ$ , whence  $[\alpha]_D + 8.6^\circ$ .

2. *1-Methylhydrindamine*.—The reaction was conducted in dry ethereal solution, and since the product was not readily soluble in ether the solvent was allowed to evaporate and the residue washed at the pump with dilute hydrochloric acid, hot water, dilute sodium carbonate, and hot water successively. The substance, which then melted at  $150$ — $152^\circ$ , was now subjected to fractional crystallisation from benzene and separated into at least eight portions, but in this case, as before, only one compound was found to be present, although the last fractions had their melting point lowered slightly through the presence of a trace of unavoidable impurity.

*d-Benzylmethylaceto-1-methylhydrindamide* crystallises from benzene and alcohol in long, silky needles very similar to those of the acid

amide of *l*-phenylethylamine and melting at  $152^{\circ}$ ; it is readily soluble in hot benzene, alcohol, chloroform, or ether.

0.4071, dissolved in chloroform and diluted to 20 c.c., gave, in a 200 mm. tube,  $\alpha - 1.08^{\circ}$ , whence  $[\alpha]_D - 26.5^{\circ}$ .

3. *l*-Menthylamine.—The optically pure base, prepared from its *d*-bromocamphorsulphonate (Tutin and Kipping, *Trans.*, 1904, 85, 65) dissolved in ether, was added to an ethereal solution of *d*-benzylmethylacetyl chloride, when a vigorous reaction occurred; the deposited menthylamine hydrochloride was separated by filtration and the ethereal solution washed with dilute hydrochloric acid, sodium carbonate, and water successively. The product was fractionally crystallised from benzene and separated into at least six fractions, but the first and last fractions were identical in crystalline form and melting point.

*d*-Benzylmethylaceto-*l*-menthylamide crystallises from benzene in long needles melting at  $140^{\circ}$ ; it is readily soluble in all the ordinary organic solvents.

0.7704, dissolved in chloroform and diluted to 20 c.c. in a 200 mm. tube, gave  $\alpha + 0.58^{\circ}$ , whence  $[\alpha]_D + 7.5^{\circ}$ .

4. *d*-Hydrindamine.—The reaction was conducted as in the case of the former active bases and the product fractionated from benzene. Six fractions were thus obtained, but no difference in appearance or melting point could be observed on comparing the first and last deposits.

*d*-Benzylmethylaceto-*d*-hydrindamide crystallises from benzene in long, colourless needles melting at  $148-149^{\circ}$ ; it is readily soluble in methyl alcohol, chloroform, acetone or ethyl acetate; moderately so in ether, and dissolves sparingly in light petroleum.

0.8580, dissolved in methyl alcohol and the solution diluted to 20 c.c., gave, in a 200 mm. tube,  $\alpha - 1.33^{\circ}$ , whence  $[\alpha]_D - 15.5^{\circ}$ .

1.2482, dissolved in chloroform and the solution diluted to 20 c.c., gave, in a 200 mm. tube,  $\alpha + 0.76^{\circ}$ , whence  $[\alpha]_D + 6.1^{\circ}$ .

#### *Action of dl-Benzylmethylacetyl Chloride on Benzoinoxime.*

*dl*-Benzoinoxime was covered with dry ether or light petroleum and slowly treated with one molecular proportion of *dl*-benzylmethylacetyl chloride. No appreciable development of heat was observed, but the gradual progress of the reaction was indicated both by the conglomeration of the benzoinoxime into a united whole, and also by the slow evolution of hydrogen chloride. If the mixture is warmed to the boiling point of the solvent, the reaction is considerably accelerated, the

whole of the oxime dissolves, and a crystalline product is deposited in small quantities.

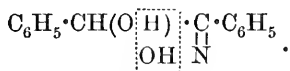
The crystalline product was fractionally crystallised from alcohol; the first deposit consisted of beautiful, long, lemon-yellow crystals which were evidently pure and melted at  $95^{\circ}$ , being thus identified as benzil. The second deposit of crystals consisted of a mixture of small, colourless needles and of a white, fluffy, crystalline substance. The latter, which was immediately dissolved on washing with water, consisted of ammonium chloride. The residue, when crystallised, yielded colourless needles identified as benzoin (m. p.  $134^{\circ}$ ). The alcoholic mother liquors yielded further quantities of these three products only.

The ethereal solution gave, on evaporation, a yellow oil, which was washed with dilute aqueous sodium carbonate until the extracts were found to be free from acid. The substance thus removed was precipitated from the alkaline solution by the addition of dilute sulphuric acid, extracted with ether, and distilled under reduced pressure (18 mm.). It consisted almost entirely of benzylmethylacetic acid, boiling at  $164^{\circ}$ . The ethereal solution, which had been extracted with sodium carbonate, gave, on evaporation, an oil, which had a strong odour of bitter almonds and which was distilled under atmospheric pressure, the fractions being collected at  $179\text{--}190^{\circ}$  and  $190\text{--}200^{\circ}$ . The residue was then distilled under reduced pressure (17 mm.) and the distillate solidified to a yellow mass, which, when crystallised from alcohol, melted at  $95^{\circ}$ , and proved to be benzil, the presence of which among the products of the reaction had been previously observed. The two fractions, boiling at  $179\text{--}190^{\circ}$  and  $190\text{--}200^{\circ}$  respectively, were too small for further fractional distillation, but as the former had the strong odour and boiling point of benzaldehyde, it was treated with phenylhydrazine in acetic acid solution, when benzaldehydephenylhydrazone (m. p.  $154^{\circ}$ ) was obtained. The second fraction, boiling at  $190\text{--}200^{\circ}$ , was found to be hydrolysed by prolonged boiling with an aqueous solution of sodium hydroxide, a copious evolution of ammonia taking place; the alkaline solution, when neutralised, yielded a crystalline precipitate, which was identified as benzoic acid. This fraction therefore consisted chiefly of benzonitrile.

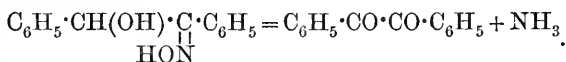
We have thus shown that the products of the interaction of benzoin-oxime and benzylmethylacetyl chloride are: (1) benzylmethylacetic acid; (2) benzaldehyde; (3) benzonitrile; (4) benzoin; (5) benzil; (6) ammonium chloride; and (7) hydrogen chloride.

This decomposition of the molecule of benzoinoxime by the acid chloride is somewhat obscure, but apparently decomposition occurs in two different directions simultaneously. In the first instance, the molecule is severed between the two central carbon atoms with the

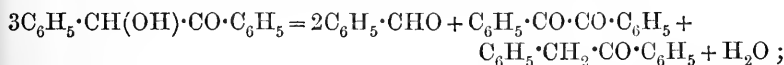
formation of benzaldehyde and its oxime, the latter of which by dehydration is converted into benzonitrile. This decomposition may be indicated thus :



In the second place, the decomposition of the benzoinoxime takes place by the elimination of ammonia and the formation of benzil according to the equation :

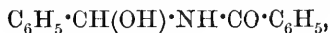


In any case, the above decomposition of benzoinoxime at the ordinary temperature is a reaction of some interest, inasmuch as it affords one of the few known examples whereby the benzoincondensation of benzaldehyde is reversed. Zinin (*Ber.*, 6, 1207), by repeated distillation of benzoin, obtained a decomposition into benzaldehyde, benzil, deoxybenzoin, and water according to the equation :

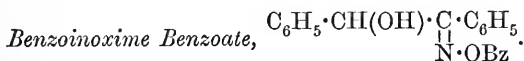


whilst the same products were obtained by passing benzoin vapour through a red-hot tube (compare also Knoevenagel and Tomaszewski (*Ber.*, 1903, 36, 2829).

Thinking that the decomposition of the benzoinoxime might be due to the action of the hydrogen chloride which is liberated, experiments were made in which an excess of dry quinoline was previously mixed with the oxime; the presence of this base, however, seemed to have little effect on the course of the reaction. It may be added that in many of the experiments the various products already enumerated were accompanied by very small quantities of a crystalline compound melting at 126°; this substance was not identified, but from its composition and reactions it seemed to be the substituted amide,



produced by intramolecular change.



In order to ascertain whether other acid chlorides would react normally with benzoinoxime giving acyl derivatives, or whether, like benzylmethylacetyl chloride, they would bring about a decomposition of the molecule, molecular proportions of benzoyl chloride and benzoinoxime were allowed to interact in ethereal solution. A gradual

evolution of hydrogen chloride occurred, but the reaction was not vigorous. After keeping for several hours at the ordinary temperature, the ethereal liquid was separated from the solid by filtration. The filtrate contained unchanged benzoyl chloride together with approximately equal proportions of benzoin and benzil. The solid product consisted chiefly of benzoinoxime benzoate, but it also contained a moderate quantity of benzoin and hydroxylamine hydrochloride. The presence of the latter was shown, after the removal of the benzoate by crystallisation, by evaporating the alcoholic mother liquors and washing the residue with water. The aqueous extract immediately reduced Fehling's solution and also gave the reactions of a chloride.

Benzoinoxime benzoate is easily purified by crystallisation from alcohol, in which it is only slightly soluble (approximately 1 part in 30 parts of boiling alcohol); it is thus obtained in leaf-like plates melting at 165—166°.

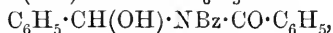
0.1540 gave 0.4301  $\text{CO}_2$  and 0.0729  $\text{H}_2\text{O}$ .  $\text{C} = 76.17$ ;  $\text{H} = 5.26$ .

0.4795 „ 19.4 c.c. moist nitrogen at 21° and 750.3 mm.  $\text{N} = 4.6$ .

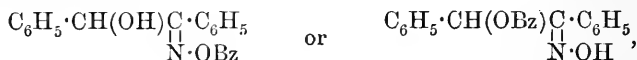
$\text{C}_{21}\text{H}_{17}\text{O}_3\text{N}$  requires  $\text{C} = 76.13$ ;  $\text{H} = 5.14$ ;  $\text{N} = 4.2$  per cent.

Benzoinoxime benzoate is hydrolysed by acids and alkalis giving benzoin, benzoic acid, and hydroxylamine. It is moderately soluble in chloroform and ethyl acetate; only slightly so in benzene.

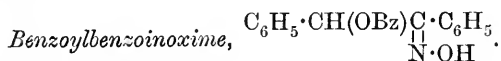
The foregoing method of preparing the benzoyl derivative leaves open several possibilities with regard to its constitution. Since benzoinoxime contains two hydroxyl groups, it is uncertain whether the benzoyl group has entered the alcoholic or the oximic hydroxyl, or whether the benzoinoxime has undergone the Beckmann transformation prior to benzoylation. The latter possibility, however, is shown to be untenable by a study of the reactions of the product. Since, on hydrolysis, it yields benzoin and hydroxylamine, it cannot have the constitution  $\text{C}_6\text{H}_5 \cdot \text{CH}(\text{OH}) \cdot \text{CO} \cdot \text{NBz} \cdot \text{C}_6\text{H}_5$  or



but may be either



A decision between these two formulæ has been rendered possible by the fact that we have prepared the compound having the latter constitution by benzoylating benzoin prior to the introduction of the oxime group, a process which ensures the substitution of the hydrogen of the alcoholic hydroxyl group by the benzoyl radicle. In order to distinguish between the two isomerides, we have described them as benzoinoxime benzoate and benzoylbenzoinoxime respectively.



Benzoylbenzoin was prepared by heating molecular proportions of benzoin and benzoyl chloride at  $150^\circ$  for an hour (Zinin, *loc. cit.*); the reaction was always accompanied by oxidation with the formation of benzil (about 10 per cent.). The benzoylbenzoin was boiled in aqueous alcoholic solution with twice the theoretical quantities of sodium acetate and hydroxylamine hydrochloride, the heating being continued during 6—12 hours; when the greater portion of the alcohol was then distilled off and the residue poured into water, the semi-solid product, on crystallisation from alcohol, deposited globular clusters of crystals melting at  $148^\circ$ .

0.2400 gave 0.1122  $\text{H}_2\text{O}$  and 0.6704  $\text{CO}_2$ .  $\text{C} = 76.18$ ;  $\text{H} = 5.19$ .

0.5295 „ 20.3 c.c. moist nitrogen at  $17.5^\circ$  and 763.5 mm.  $\text{N} = 4.5$ .

$\text{C}_{21}\text{H}_{17}\text{O}_3\text{N}$  requires  $\text{C} = 76.13$ ;  $\text{H} = 5.14$ ;  $\text{N} = 4.2$  per cent.

Benzoylbenzoinoxime is readily soluble in the ordinary organic solvents.

#### *Action of Benzylmethylacetyl Chloride on $\alpha$ -Benzaldoxime.*

When  $\alpha$ -benzaldoxime, covered with light petroleum, is treated with benzylmethylacetyl chloride, the mixture becomes warm and hydrogen chloride is slowly evolved, while the transparent crystals of the oxime are converted into a fine, white powder. After leaving the mixture at the ordinary temperature for several hours, the solid is separated by filtration and identified as benzamide. On evaporation, the light petroleum solution gave an oil which had a strong odour of bitter almonds; on distilling in steam, a portion passed over and was identified as benzonitrile. The residue consisted of benzylmethylacetic acid.

In one experiment, 10.7 grams of acid chloride and 7.1 grams of benzaldoxime were used, from which 5 grams of benzonitrile, 2 grams of benzamide, and 9 grams of benzylmethylacetic acid were obtained.

In a second experiment, only 0.5 gram of benzamide was produced from 8.3 grams of benzaldoxime, with a corresponding increase in the quantity of benzonitrile.

#### *The Resolution of dl-Bases with the Aid of an Active Acid Chloride.*

##### *Action of d-Benzylmethylacetyl Chloride on dl-Hydrindamine.*

On slowly adding a dry ethereal solution of hydrindamine (2 mols.) to an ethereal solution of benzylmethylacetyl chloride (1 mol.), pre-

pared from the *d*-acid in the ordinary way, a vigorous reaction ensues with development of heat and precipitation of hydrindamine hydrochloride, but after about half the base has been run in, the reaction moderates considerably. The solution, left overnight to ensure complete interaction, is then washed with water, the ether allowed to evaporate, and the crystalline product separated by filtration and washed with water until free from hydrochloride. On repeatedly crystallising the crude hydrindamide from methyl alcohol, the most sparingly soluble isomeride is obtained without much trouble; this compound crystallises from methyl alcohol in colourless needles or prisms melting at 148—149°; it is readily soluble in cold methyl alcohol, ethyl acetate, ether, and acetone, but practically insoluble, even in boiling water. This compound is laevorotatory in methyl-alcoholic solution, and is a derivative of *d*-hydrindamine, as is proved by the fact that it is identical with the *d*-benzylmethylaceto-*d*-hydrindamide already described (p. 449); its specific rotation was determined with the following results:

0.5766, in 25 c.c. methyl alcohol and in a 200 mm. tube, gave  $\alpha - 0.74^\circ$ , whence  $[\alpha]_D - 16^\circ$ .

0.1411 gave 0.4232 CO<sub>2</sub> and 0.0952 H<sub>2</sub>O. C = 81.79; H = 7.5.

0.1419 „ 0.4266 CO<sub>2</sub> „ 0.1016 H<sub>2</sub>O. C = 82.0; H = 7.9.

C<sub>19</sub>H<sub>21</sub>ON requires C = 81.7; H = 7.5 per cent.

The various mother liquors remaining after the isolation of the *d*-benzylmethylaceto-*d*-hydrindamide gave crystalline deposits, which, when submitted to fractional crystallisation, gave long, ill-defined needles melting at 119—120°; this substance is one of the externally compensated compounds identical with that prepared from *dl*-hydrindamine and the *dl*-acid chloride (p. 444). The later crystalline deposits yielded a compound which crystallised from methyl alcohol in well-defined prisms melting at 110—111°; this is the isomeric externally compensated compound previously described. The mother liquors which then remained gave crystalline deposits of very indefinite melting point, and from which, owing to their very great solubility, it seemed impossible to isolate the last component of the original product, namely, the derivative of the other active base. In these circumstances, the several most soluble deposits were collected, recrystallised until colourless, and then examined polarimetrically in methyl alcohol solution, when it was proved that these fractions contain a compound which was *dextro*-rotatory, and which therefore represents the derivative of the other active base, namely, the *l*-isomeride.

The acid chloride used in the above experiments had been distilled under reduced pressure, and contained a considerable quantity of the *l*-compound; the experiment was repeated, using the *d*-chloride pre-

pared as described in this paper (p. 447). In this case, the active amide melting at 148—149° was very easily isolated by two or three crystallisations from benzene, but again it was found almost impossible to obtain any quantity of a pure preparation of the isomeride from the mother liquors, although a few crystals were obtained melting at 113°. Attempts to hydrolyse the amide melting at 148—149° were unsuccessful; it seems to be quite stable towards boiling concentrated aqueous or alcoholic potash or aqueous baryta, and is only very slowly hydrolysed by boiling hydrochloric or dilute sulphuric acids, giving mere traces of ammonia and of indene; more concentrated sulphuric acid at 150° is much more rapid in its action, but ammonia is the only basic product; the liberated *d*-benzylmethylacetic acid is still optically active, thus indicating the stability of the asymmetric carbon group in this compound. The active hydrindamide, when heated in sealed tubes with alcoholic potash, hydrochloric acid, or sulphuric acid, or other hydrolysing agents, was decomposed into indene and ammonia.

*Action of d-Benzylmethylacetyl Chloride on dl-α-Phenylethylamine.*

The optically pure chloride of the *d*-acid was treated in dry ethereal solution with excess of freshly distilled base in the same solvent; a vigorous reaction took place, heat being developed, and a bulky precipitate of the hydrochloride being formed. The ether was allowed to evaporate, and the residue heated with a little water to dissolve the salt formed, when a white, slightly viscid solid remained, which melted at 95—100°. The product was first crystallised from methyl alcohol; the sparingly soluble fraction, which separated in thick prisms, melted at 118—119°; this portion was first crystallised from light petroleum (b. p. 60—80°), in which it was very sparingly soluble, and then from benzene; the fine, long needles thus obtained melted at 119°, and were identical with those of the *d*-benzylmethylaceto-*l*-phenylethylamide previously described (p. 448).

0.2925, dissolved in 25 c.c. ether gave, in a 200 mm. tube,  $\alpha + 0.24^\circ$ , whence  $[\alpha]_D + 10.3^\circ$ .

The isomeric derivative of *d*-phenylethylamine was not isolated from the mother liquors, since it was found impossible to regain the active bases by the hydrolysis of their amides.

A part of the expense incurred in this investigation has been met by a grant kindly awarded by the Government Grant Committee of the Royal Society.

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# L.—Contributions to the Knowledge of the $\beta$ -Diketones.

By SIEGFRIED RUHEMANN and EDWIN ROY WATSON.

SOME years ago, J. Wislicenus (*Annalen*, 1899, 308, 219) published the results of the work undertaken by him in conjunction with Löwenheim, Schmidt, and Wells on the interaction of alcoholic potash with benzylideneacetophenone dibromide. They found that the compound thus formed had the formula  $C_{15}H_{12}O_2$ , and they regarded it as the tautomeride of dibenzoylmethane, which had been first obtained by v. Baeyer and Perkin (*Ber.*, 1883, 16, 2134) by boiling ethyl dibenzoylacetate with water, and afterwards by Claisen (*Annalen*, 1896, 291, 52) by the action of sodium ethoxide or metallic sodium on a mixture of ethyl benzoate and acetophenone. The two tautomeric forms of dibenzoylmethane could be represented by the following formulæ:  $C_6H_5 \cdot C(OH) : CH \cdot CO \cdot C_6H_5$  and  $C_6H_5 \cdot CO \cdot CH_2 \cdot CO \cdot C_6H_5$ .

Wislicenus is inclined to regard his compound as the diketonic form, and the old dibenzoylmethane as the enol-ketonic form, because, whilst the latter dissolves in alkali with the greatest ease and yields with ferric chloride a violet-red coloration and a greyish-green precipitate with alcoholic copper acetate solution, the former is insoluble in alkali and neither gives at once a coloration with ferric chloride, nor is precipitated by copper acetate.

That Wislicenus's compound was a tautomeride of the long-known dibenzoylmethane seemed to follow from the fact that it gave the same compounds on treatment with bromine, hydroxylamine, phenylhydrazine, hydrazine, or semicarbazide. Wislicenus further showed that, although his compound remained unchanged on distillation or on boiling with acetic acid, it was transformed into the old dibenzoylmethane under the influence of mineral acids. He therefore succeeded in effecting a transformation of his compound into the other, although the reverse change could not be accomplished.

That the transformation of the one form into the other is not brought about either by boiling or under the influence of alkali seems to be incompatible with our present knowledge of tautomeric compounds. These difficulties seem to have been recognised by Wislicenus himself, for he suggested the possibility of representing his compound as benzoylphenylethylene oxide,  $C_6H_5 \cdot CO \cdot CH \cdot CH \cdot C_6H_5$ .

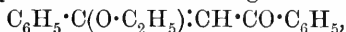


These discrepancies and the desire to prepare ketones of the acetylene series in order to examine whether they are transformed by the action of bases into heterocyclic compounds, similar to those formed

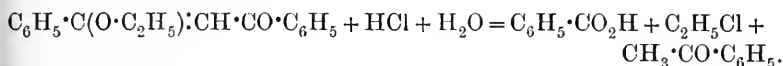
from the esters of the acetylene series (Ruhemann and Stapleton, *Trans.*, 1900, 67, 239), have induced us to repeat Wislicenus's experiments.

Such ketones of the acetylene series have indeed been obtained by Nef (*Annalen*, 1899, 308, 264) from the sodium compounds of the hydrocarbons of the acetylene series under the influence of acid chlorides; yet it seemed to us possible to prepare them from the olefinic ketones, just as Claisen has prepared acetylenic aldehydes from their olefinic analogues (*Ber.*, 1903, 36, 3664).

In following Wislicenus's directions, we obtained by the action of alcoholic potash on benzylideneacetophenone dibromide a compound with precisely the same properties as those recorded by this author for his dibenzoylmethane, but our analytical results differed considerably from the numbers given by Wislicenus, and agree, not with the formula  $C_{15}H_{12}O_2$  for dibenzoylmethane, but with  $C_{17}H_{16}O_2$ . This formula, which was, moreover, verified by a molecular weight determination, would correspond with the following constitution,



according to which the substance appears to be the ethyl ether of dibenzoylmethane, and would therefore be analogous to the corresponding esters which have lately been obtained by Lees (*Trans.*, 1903, 83, 145). This constitution is supported by the fact that the compound  $C_{17}H_{16}O_2$ , on heating with hydrochloric acid, is decomposed, giving acetophenone, benzoic acid, and ethyl chloride. This reaction, therefore, takes place in accordance with the following equation:



Löwenheim, who effected the decomposition of the compound by means of concentrated caustic potash and obtained acetophenone and benzoic acid, did not observe the formation of alcohol.

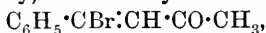
The correctness of the formula,  $C_{17}H_{16}O_2$ , for this compound is, moreover, supported by the fact that *p*-nitrobenzylideneacetophenone dibromide, on treatment with alcoholic potash, yields the corresponding nitro-derivative,  $C_{17}H_{15}(NO_2)O_2$ , which, therefore, is to be regarded as the ethyl ether of *p*-nitrodibenzoylmethane,



As regards the formation of the ethyl ether of dibenzoylmethane from benzylideneacetophenone dibromide, there cannot be any doubt that the first action of the alcoholic potash is to remove 1 mol. of hydrogen bromide and to yield the bromobenzylideneacetophenone,



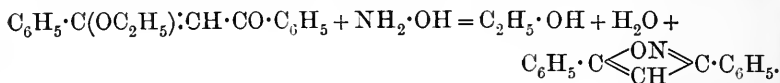
a compound obtained by Schmidt (Wislicenus, *loc. cit.*) by the action of potassium acetate on the dibromide. We have obtained a similar compound, namely, bromobenzylideneacetone,



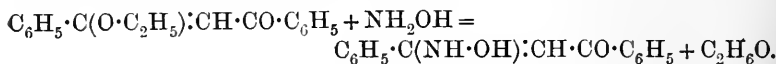
by the action of alcoholic potash in the cold on the benzylideneacetone dibromide. The bromobenzylideneacetophenone is subsequently transformed into the ethyl ether of dibenzoylmethane, either by the further removal of hydrogen bromide and subsequent union of alcohol with the first formed benzoylphenylacetylene, or by the direct replacement of the bromine atom by the ethoxyl group.

This constitution shows why the compound is insoluble in aqueous caustic potash and does not give a coloration with ferric chloride or a precipitate with copper acetate. It further explains why the compound can be readily transformed into dibenzoylmethane, and why the reverse change cannot be directly effected. Moreover, all the reactions of this compound, as described by Wislicenus, can be readily explained on this view of its constitution.

For example, an  $\alpha\gamma$ -diphenylisooxazole is formed with hydroxylamine,



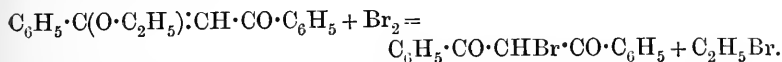
The formation of  $\alpha\gamma$ -diphenylisooxazole, as shown by Wislicenus (*loc. cit.*), is preceded by that of a compound which he regarded as an oxime of dibenzoylmethane. The fact, however, that this substance, which is produced also from v. Baeyer and Perkin's dibenzoylmethane, does not yield a coloration with ferric chloride, is not in harmony with the formula  $\text{C}_6\text{H}_5\cdot\text{C}(\text{OH}):\text{CH}\cdot\text{C}(\text{C}_6\text{H}_5):\text{NOH}$ . After having proved that Wislicenus's dibenzoylmethane is ethoxybenzylideneacetophenone, its reaction with hydroxylamine may be expressed as follows:



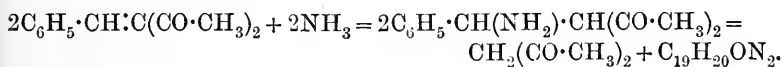
The compound would thus appear to be a hydroxylamine derivative and not an oxime. This constitution agrees with the fact that the compound does not give a coloration with ferric chloride; it explains, also, why the substance, although unchanged by neutral solvents, is readily transformed into  $\alpha\gamma$ -diphenylisooxazole under the influence of alkalis. It is thus isomerised to  $\text{C}_6\text{H}_5\cdot\text{C}(:\text{NOH})\cdot\text{CH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_5$ , which subsequently loses water to form the isooxazole derivative.

A ready explanation is also afforded of the action of bromine in forming the monobromo- and dibromo-benzoylmethane compounds, previously

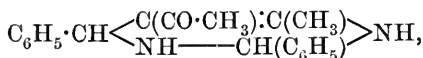
prepared by Neufville and v. Pechmann (*Ber.*, 1890, 23, 3377) from dibenzoylmethane,



In connection with this investigation, we record the result of our experiments on the behaviour of bases towards olefinic diketones, an account of the action of benzamidine on these diketones having been lately given (*Trans.*, 1903, 83, 1371). The results obtained induced us to examine also the action of other bases on these diketones. We find that ammonia readily reacts with benzylideneacetylacetone, yielding a compound having the formula  $\text{C}_{19}\text{H}_{20}\text{ON}_2$ , the formation of which may be thus represented :

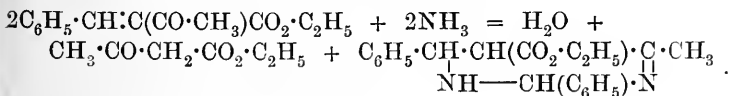


The constitution of the product should probably be expressed as follows :



according to which it is to be regarded as acetyldiphenylmethyltetrahydropyrimidine. This constitution is in agreement with the fact that the compound, although readily decomposed by dilute mineral acids with the formation of benzaldehyde, is yet comparatively stable towards alkalis. On heating with alkali, no ammonia is evolved, but on removing the acetyl group a compound is formed which is probably the corresponding diphenylmethyltetrahydropyrimidine.

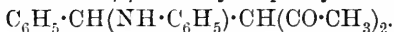
One of us (Ruhemann, *Trans.*, 1903, 83, 378) has shown that by the action of ammonia on ethyl benzylideneacetoacetate, a compound was formed which was regarded as benzylideneaminoacetone,  $\text{C}_{10}\text{H}_{11}\text{ON}$ . On account of the ease with which this substance is decomposed, the above formula could not be verified by a molecular weight determination. The behaviour of this compound is analogous to that of the substance obtained from benzylideneacetylacetone, and this makes it necessary to assign to the two compounds similar constitutions. Such considerations lead us to double the molecular weight of the compound obtained from ethyl benzylideneacetoacetate, and to regard it as ethyl diphenylmethyltetrahydropyrimidinecarboxylate. Its formation may then be expressed by the following equation :



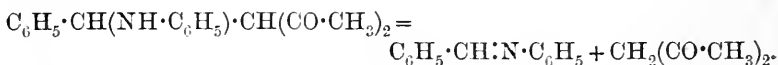
These compounds are still under examination.

The assumption that the first step in the reaction of ammonia on benzylideneacetylacetone leads to the formation of an additive product, as indicated in the above equation, is rendered probable by the action of aniline on benzylideneacetylacetone.

These compounds interact at the ordinary temperature to form the additive product,  $\alpha$ -anilino- $\beta\beta$ -diacetyl- $\alpha$ -phenylethane,

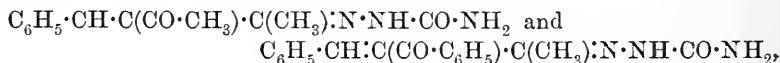


This compound, however, on heating at  $100^\circ$ , decomposes with the formation of benzylideneaniline and acetylacetone according to the equation:

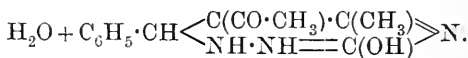
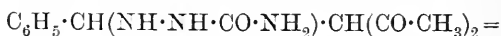
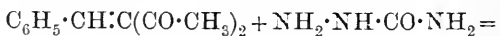


Phenylhydrazine reacts with benzylideneacetylacetone as well as with benzylidenebenzoylacetone with development of heat, but the additive products, which may be assumed to be first formed, cannot be isolated, since, in both cases, they at once decompose forming benzaldehydephenylhydrazone.

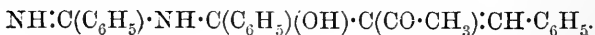
The action of semicarbazide on benzylideneacetylacetone and benzylidenebenzoylacetone is of especial interest; in both cases, the reaction takes place between 1 mol. of the olefinic diketone and 1 mol. of the semicarbazide; water (1 mol.) is eliminated, and compounds are obtained having the formulæ  $\text{C}_{13}\text{H}_{15}\text{O}_2\text{N}_3$  and  $\text{C}_{18}\text{H}_{17}\text{O}_2\text{N}_3$  respectively. These compounds might be regarded as semicarbazones,



but taking into consideration the behaviour of other bases towards the olefinic diketones, there remains the alternative view that, in these cases also, additive products are first formed, which subsequently lose water to form cyclic compounds, for example:



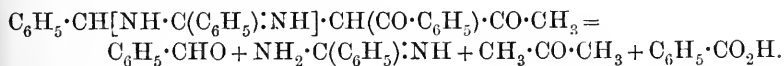
One of us has recently shown (*loc. cit.*) that benzamidine also reacts with benzylidenebenzoylacetone forming an additive product. The fact that this compound, on heating with hydrochloric acid, decomposes and yields dibenzamide led to the view that the constitution of this compound should be represented by the formula:



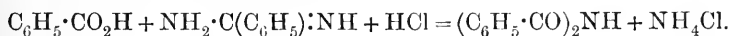
This constitution, however, would not be in harmony with the results recorded in this paper, according to which the bases react additively with the olefinic diketones in such a way as to destroy the double linking. In the light of these researches, the above compound must be represented thus :



and this formula would also readily explain the formation of dibenzamide. Under the influence of hydrochloric acid, decomposition takes place, as indicated by the equation :



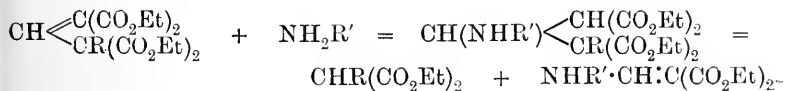
The benzamidine and benzoic acid in turn react in the presence of mineral acid to yield dibenzamide, thus :



The reaction of benzamidine on benzylideneacetylacetone, which, as has been shown lately (*loc. cit.*), yields diphenylmethyl dihydropyrimidine, may well be explained in a similar manner by assuming that first the additive product,  $\text{C}_6\text{H}_5 \cdot \text{CH}[\text{NH} \cdot \text{C}(\text{C}_6\text{H}_5) : \text{NH}] \text{CH}(\text{CO} \cdot \text{CH}_3)_2$ , is formed, which then condenses to the dihydropyrimidine.

The constitution of the products formed by the interaction of benzylideneacetylacetone and benzylidenebenzoylacetone with semicarbazide has not yet been definitely fixed, but without considering this problem the general hypothesis may be deduced that, in the first place, ammonia and organic bases, on reacting with the olefinic diketones, destroy the ethylene linking to form additive compounds.

This assumption may be extended to explain the behaviour of bases towards ethyl dicarboxyglutaconate and its derivatives. As shown by one of us and his pupils, ethyl benzyl dicarboxyglutaconate, on treatment with ammonia, yields ethyl benzyl malonate and ethyl aminomethylenemalonate. In these cases, also, it may be supposed that the decomposition is preceded by the formation of additive products, which subsequently break up in the manner indicated by the following equation :



## EXPERIMENTAL.

*Action of Alcoholic Potash on Benzylideneacetophenone Dibromide.*

Benzylideneacetophenone is readily prepared by Claisen's method (*Ber.*, 1887, 20, 657) by the action of sodium methoxide in methyl-alcoholic solution on a mixture of benzaldehyde and acetophenone. Its transformation into the dibromide,  $C_6H_5 \cdot CHBr \cdot CHBr \cdot CO \cdot C_6H_5$ , is best effected by dissolving the olefinic ketone in carbon disulphide instead of chloroform, as recommended by Wislicenus (*loc. cit.*), when almost the total quantity of the dibromide separates out; it dissolves in boiling alcohol with difficulty and, on cooling, crystallises in colourless needles which melt at  $158^\circ$  (according to Wislicenus at  $156.5-157.5^\circ$ ).

0.2078 gave 0.3711  $CO_2$  and 0.0642  $H_2O$ . C = 48.70; H = 3.43.

0.2017 „ 0.3618  $CO_2$  „ 0.0624  $H_2O$ . C = 48.92; H = 3.43.

0.2371 „ 0.2406 AgBr. Br = 43.18.

$C_{15}H_{12}OBr_2$  requires C = 48.91; H = 3.26; Br = 43.47 per cent.

We have pointed out in the introduction that the dibromide reacts with alcoholic potash to yield the ethyl ether of dibenzoylmethane,  $C_6H_5 \cdot C(O \cdot C_2H_5) : CH \cdot CO \cdot C_6H_5$ , instead of dibenzoylmethane,



as stated by Wislicenus. Our mode of procedure is practically the same as employed by this author: caustic potash (2 mols.) dissolved in absolute alcohol is gradually added to the hot solution of the dibromide (1 mol.) in absolute alcohol, and the reaction is completed by digesting the mixture at  $100^\circ$  for about an hour. The alcohol is then distilled from the water-bath as far as possible, the residue treated with water and extracted with ether. After drying the ethereal solution with calcium chloride and evaporating off the ether, an oil is left which distils at  $212^\circ$  under 10 mm. pressure. The yellowish, oily distillate, when left for a short time, solidifies almost completely. The solid is only sparingly soluble in cold light petroleum (b. p.  $50-80^\circ$ ), but readily dissolves in the hot solvent. It is readily soluble in hot alcohol and crystallises from either solvent in colourless prisms which melt at  $77-78^\circ$  and have all the properties recorded by Wislicenus for his "dibenzoylmethane."

0.2037 gave 0.6020  $CO_2$  and 0.1190  $H_2O$ . C = 80.60; H = 6.49.

0.1925 „ 0.5695  $CO_2$  „ 0.1120  $H_2O$ . C = 80.68; H = 6.46.

0.1818 „ 0.5397  $CO_2$  „ 0.1052  $H_2O$ . C = 80.96; H = 6.42.

$C_{17}H_{16}O_2$  requires C = 80.95; H = 6.35 per cent.

These numbers differ considerably from those given by J. Wislicenus, which show a close agreement with the percentage results required for dibenzoylmethane,  $C_{15}H_{12}O_2$ , namely, C = 80.36 ; H = 5.36 per cent.

The formula  $C_{17}H_{16}O_2$  agrees also with the result of the molecular weight determination of the compound by the freezing point method.

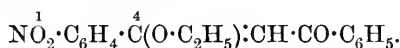
0.405 in 22.49 benzene gave  $\Delta t = 0.405^\circ$ . M. W. = 256.

$C_{17}H_{16}O_2$  requires M. W. = 252.

The constitution  $C_6H_5 \cdot C(O \cdot C_2H_5) : CH \cdot CO \cdot C_6H_5$  follows from the decomposition which the compound undergoes when heated with concentrated hydrochloric acid in a closed tube at  $150-160^\circ$  for two hours. It thus furnishes ethyl chloride, acetophenone, and benzoic acid. The formation of ethyl chloride is sufficiently proved by the fact that on opening the cold tube hardly any pressure is noticed, but on warming, a gas escapes which burns with a green flame. The other products of decomposition have been isolated and identified as acetophenone and benzoic acid by their properties and by analysis.

*Action of Alcoholic Potash on p-Nitrobenzylideneacetophenone Dibromide.*

The action of alcoholic potash on benzylideneacetophenone dibromide is analogous to the behaviour of the same reagent towards the *p*-nitrobenzylideneacetophenone dibromide, the latter reaction giving rise to the ethyl ether of *p*-nitrodibenzoylmethane :



*p*-Nitrobenzylideneacetophenone is formed by adding dilute caustic soda to an alcoholic solution of *p*-nitrobenzaldehyde and acetophenone. It was thus prepared by Sorge (*Ber.*, 1902, 35, 1068), who also transformed it into the dibromide. We find that the union of bromine with the olefinic ketone takes place more readily than stated by this investigator, and that it is completed when the solution of both reagents in chloroform has been left overnight. The dibromide, which separates out on concentrating the solution, has been once recrystallised from chloroform, when it is obtained in yellow needles. On gradually adding the exact quantity of alcoholic potash (2 mols.) dissolved in absolute alcohol to the hot alcoholic solution of *p*-nitrobenzylideneacetophenone dibromide (1 mol.), potassium bromide separates out and the solution turns deep red. After digesting the mixture for an hour at  $100^\circ$ , the alcohol is distilled from the water-bath and the residue extracted with ether. On evaporating off the ether, a dark oil is left behind which partially solidifies in the course of 2—3 days ; the solid is collected at the pump and dissolved in hot dilute alcohol, from which solvent it separates in yellow needles which,

after two crystallisations from the same solvent, melt constantly at 89—90°.

0.1993 gave 0.5018 CO<sub>2</sub> and 0.0923 H<sub>2</sub>O. C = 68.62; H = 5.14.

0.1965 „ 8.4 c.c. moist nitrogen at 17° and 744.5 mm. N = 4.85.

0.1959 „ 8.4 c.c. „ at 19° and 755.5 mm. N = 4.89.

C<sub>17</sub>H<sub>15</sub>O<sub>4</sub>N requires C = 68.68; H = 5.05; N = 4.71 per cent.

*p*-Nitrodibenzoylmethane is readily soluble in alcohol, chloroform, or ether and insoluble in cold potash, but on warming with the alkali, however, decomposition takes place, and the odour of acetophenone is perceptible.

*Action of Alcoholic Potash on the Benzylideneacetone Dibromide.*

In preparing benzylideneacetone, we have followed the directions given by Claisen and Ponder (*Annalen*, 1884, 223, 139). This compound readily takes up bromine and yields the dibromide, C<sub>6</sub>H<sub>5</sub>·CHBr·CHBr·CO·CH<sub>3</sub>, but for this purpose we find it advisable to employ carbon disulphide rather than chloroform as a solvent (compare Claisen and Claparède, *Ber.*, 1881, 14, 2461), since the yield is better and the product is at once obtained in a pure state. On adding caustic potash (2 mols.), dissolved in absolute alcohol, to the warm alcoholic solution of the dibromide (1 mol.), potassium bromide separates, and the solution turns red without further heating. The alcohol was not distilled off, as in the previous cases, but the solution was diluted with water and extracted with ether. After removing the ether, a yellow oil was obtained boiling at 150—151° and 169—170° under 10 and 20 mm. pressure respectively.

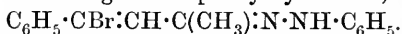
This compound was bromobenzylideneacetone, C<sub>6</sub>H<sub>5</sub>·CBr:CH·CO·CH<sub>3</sub>, which, however, as indicated by the analysis, was not quite pure, but probably contained a little of the ethyl ether of benzoylacetyl-methane.

0.2063 gave 0.4023 CO<sub>2</sub> and 0.0839 H<sub>2</sub>O. C = 53.18; H = 4.51.

0.2264 „ 0.1775 AgBr. Br = 33.39.

C<sub>10</sub>H<sub>9</sub>OBr requires C = 53.33; H = 4.0; Br = 35.55 per cent.

On adding phenylhydrazine to the alcoholic solution of bromobenzylideneacetone and slightly warming, a crystalline precipitate slowly separates, consisting of the phenylhydrazone,



This substance crystallises from alcohol in yellow, glistening plates which melt and decompose at 97°.

0.1831 gave 14.2 c.c. moist nitrogen at 20° and 763 mm. N = 8.90.

C<sub>16</sub>H<sub>15</sub>N<sub>2</sub>Br requires N = 8.89 per cent.

Bromobenzylideneacetone is analogous to the bromobenzylideneacetophenone,  $C_6H_5 \cdot CBr \cdot CH \cdot CO \cdot C_6H_5$ , which Schmidt (*loc. cit.*) obtained by the action of potassium acetate on benzylideneacetophenone dibromide. We have as yet not heated the bromobenzylideneacetone with alcoholic potash, but we propose to carry out this experiment with the view of examining whether in this case the corresponding ethyl ether,  $C_6H_5 \cdot C(O \cdot C_2H_5) \cdot CH \cdot CO \cdot CH_3$ , of acetylbenzoylmethane is produced.

*Action of Ammonia and Organic Bases on Olefinic Diketones.*

One of us has shown lately (Trans., 1903, 83, 1371) that, in the first place additive products are formed by the action of benzamidine on these diketones, and such a product has been isolated on treating benzamidine with benzylidenebenzoylacetone. We have already stated (p. 459) that other bases form with these diketones similar additive products, which, however, are unstable and readily give rise to other compounds.

*Action of Ammonia on Benzylideneacetylacetone and Benzylidenebenzoylacetone.*

The solution of benzylideneacetylacetone in excess of alcoholic ammonia, when left overnight, deposits colourless plates. These are insoluble in ether, but readily dissolve in hot alcohol and melt somewhat indefinitely at  $147^\circ$ .

0.2010 gave 0.5739  $CO_2$  and 0.1248  $H_2O$ .  $C = 77.87$ ;  $H = 6.89$ .

0.1844 „ 15.4 c.c. moist nitrogen at  $12^\circ$  and 749 mm.  $N = 9.71$ .

0.1865 „ 15.4 c.c. „ „ „  $15^\circ$  and 755 mm.  $N = 9.66$ .

$C_{19}H_{20}ON_2$  requires  $C = 78.08$ ;  $H = 6.85$ ;  $N = 9.59$  per cent.

With regard to the constitution of this compound, we have already (p. 459) expressed the view that it is acetyldiphenylmethyltetrahydropyrimidine. It dissolves in cold dilute mineral acids, but on warming the solution, decomposition takes place, which is indicated by the formation of benzaldehyde. The compound is more stable towards alkalis for, on boiling with alcoholic potash, no odour of benzaldehyde is perceptible, but it loses the acetyl group and yields a substance which is most probably diphenylmethyltetrahydropyrimidine. This product is isolated by distilling off the alcohol from the water-bath and adding water to the residue; a yellow oil is thus precipitated, whilst the aqueous solution contains acetic acid, which has been identified by its general reactions. The oil, which rapidly solidifies and crystallises from dilute alcohol in yellow leaflets, is still under examination.

The action of alcoholic ammonia on benzylidenebenzoylacetone differs from the preceding condensation. In this case, the solution turned yellow, but did not deposit a solid, even after a long time. On adding water to the solution, a viscous product was precipitated which could not be induced to crystallise.

*Action of Aniline on Benzylideneacetylacetone.*

A mixture of equal quantities of benzylideneacetylacetone and aniline, when left for a short time, develops heat and becomes solid. After washing with a little alcohol, the product is dissolved in hot dilute alcohol; the solution, on cooling, deposits colourless needles which melt at  $113^{\circ}$ .

0.2010 gave 0.5646  $\text{CO}_2$  and 0.1248  $\text{H}_2\text{O}$ .  $\text{C} = 76.60$ .  $\text{H} = 6.89$ .

0.2367 „ 11 c.c. moist nitrogen at  $22^{\circ}$  and 732 mm.  $\text{N} = 5.04$ .

0.2384 „ 11 c.c. „ „ „  $21^{\circ}$  and 733 mm.  $\text{N} = 5.03$ .

$\text{C}_{18}\text{H}_{19}\text{O}_2\text{N}$  requires  $\text{C} = 76.86$ ;  $\text{H} = 6.76$ ;  $\text{N} = 4.98$  per cent.

This additive compound,  $\text{C}_6\text{H}_5 \cdot \text{CH}(\text{NH} \cdot \text{C}_6\text{H}_5) \cdot \text{CH}(\text{CO} \cdot \text{CH}_3)_2$ , is somewhat unstable, and when heated on the water-bath it readily decomposes into acetylacetone and benzylideneaniline. This mixture, on cooling, partially solidifies; the adhering oil is pressed out from the solid, and the latter dissolved in hot dilute alcohol. On cooling, a white emulsion is produced in the solution, which gradually deposits a compound crystallising in colourless plates melting at  $50$ — $51^{\circ}$ . This compound was identified as benzylideneaniline by the foregoing properties and by analysis.

The additive compound is also formed on heating the mixture of aniline and benzylideneacetylacetone at  $100^{\circ}$ .

*Action of Phenylhydrazine on Benzylideneacetylacetone and Benzylidenebenzoylacetone.*

On mixing benzylideneacetylacetone (3 grams) and phenylhydrazine (2 grams), heat was developed and a semi-solid product results, which crystallised from dilute alcohol in almost colourless needles melting at  $155$ — $156^{\circ}$ , and was identified by these properties and by analysis as benzaldehydephenylhydrazone.

Benzylidenebenzoylacetone reacts with phenylhydrazine in a similar manner; an alcoholic solution of these reagents, when boiled and subsequently cooled, deposits needles melting at  $155$ — $156^{\circ}$ .

0.2069 gave 0.6010  $\text{CO}_2$  and 0.1165  $\text{H}_2\text{O}$ .  $\text{C} = 79.26$ ;  $\text{H} = 6.25$ .

0.2032 „ 25.5 c.c. moist nitrogen at  $16^{\circ}$  and 743 mm.  $\text{N} = 14.29$ .

$\text{C}_{13}\text{H}_{12}\text{N}_2$  requires  $\text{C} = 79.59$ ;  $\text{H} = 6.12$ ;  $\text{N} = 14.28$  per cent.

*Action of Semicarbazide on Benzylideneacetylacetone and on Benzylidenebenzoylacetone.*

Semicarbazide hydrochloride (1 mol.), dissolved in water, is mixed with a solution of sodium (1 atom) in alcohol, and then treated with benzylideneacetylacetone (1 mol.); heat is developed, and after a short time a precipitate is formed which dissolves in alcohol with difficulty and, on cooling, crystallises in yellow plates, which melt at  $210^{\circ}$  with evolution of gas.

0.2030 gave 0.4728  $\text{CO}_2$  and 0.1147  $\text{H}_2\text{O}$ .  $\text{C} = 63.52$ ;  $\text{H} = 6.27$ .

0.1604 „ 24.5 c.c. moist nitrogen at  $18^{\circ}$  and 746.5 mm.  $\text{N} = 17.31$ .

$\text{C}_{13}\text{H}_{15}\text{O}_2\text{N}_3$  requires  $\text{C} = 63.67$ ;  $\text{H} = 6.12$ ;  $\text{N} = 17.14$  per cent.

Benzylidenebenzoylacetone reacts with semicarbazide under the same conditions. The white, crystalline precipitate which separates is insoluble in water, sparingly soluble in boiling alcohol, and melts at  $230^{\circ}$  with evolution of gas. For analysis, the compound was washed successively with water and alcohol.

0.2013 gave 0.5174  $\text{CO}_2$  and 0.1034  $\text{H}_2\text{O}$ .  $\text{C} = 70.10$ ;  $\text{H} = 5.70$ .

0.1679 „ 19.5 c.c. moist nitrogen at  $9^{\circ}$  and 744.5 mm.  $\text{N} = 13.68$ .

$\text{C}_{18}\text{H}_{17}\text{O}_2\text{N}_3$  requires  $\text{C} = 70.35$ ;  $\text{H} = 5.53$ ;  $\text{N} = 13.68$  per cent.

Further experiments are required in order to decide whether these substances are cyclic compounds, as indicated in the introduction, or whether they are mono-semicarbazones of benzylideneacetylacetone and benzylidenebenzoylacetone, but at present we are inclined to hold the latter view.

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## LI.—*The Formation of Periodides in Organic Solvents.*

By HARRY MEDFORTH DAWSON.

THE results of an investigation on the nature of nitrobenzene solutions containing iodine and potassium iodide have been already communicated to the Society (Dawson and Gawler, *Trans.*, 1902, 81, 524). It was found that solutions containing small quantities of iodine, when saturated with potassium iodide, dissolve approximately one molecular proportion of the latter for each molecule of iodine present. With more concentrated iodine solutions, the proportion of potassium iodide dissolved is smaller. On the other hand, solutions saturated with iodine contain four molecules of iodine for each molecule of iodide present, and this relationship holds for a very

extended series of concentrations. The existence in solution of complex periodides represented by  $KI_3$  and  $KI_5$  was deduced from these experiments.

The considerable solvent action thus exhibited by nitrobenzene for these periodides, taken in conjunction with the fact that potassium iodide alone is practically insoluble and iodine only moderately soluble (0.2 gram-mol. per litre) in nitrobenzene, seemed to justify a closer inquiry into the cause of this phenomenon. The nitro-group is possibly a factor in promoting the formation of the dissolved periodides for the free hydrocarbon and many substituted benzene derivatives do not dissolve any appreciable amount of potassium iodide even in the presence of iodine. With this idea as a working hypothesis, several other nitro-compounds have been examined, but since the great majority of these derivatives are solid at the ordinary temperature the number available for direct investigation is somewhat limited.

Nitrobenzene was replaced by the liquid nitro-compounds, *o*-nitrotoluene, *m*-nitrotoluene, *o*-nitroanisole, nitromethane, nitropentane, and trichloronitromethane. In none of these solvents is potassium iodide sensibly soluble, whilst iodine only dissolves to a comparatively small extent.

In the first series of solubility measurements, the results of which are recorded in the following table, the quantities of potassium iodide dissolved by solutions containing varying amounts of iodine were determined; in the second series, the solubility of iodine in solutions containing potassium iodide in varying amounts was measured:

*Composition of Solutions saturated with Potassium Iodide.*

Solvent.	Iodine concentration.		Potassium iodide concentration.		Molecular Ratio $I_2/KI$ .
	Grams.	Gram-mols.	Grams.	Gram-mols.	
<i>o</i> -Nitrotoluene .....	183	0.721	89.4	0.539	1.34
„ .....	429	1.69	158.5	0.955	1.77
„ .....	753	2.97	221	1.33	2.23
<i>m</i> -Nitrotoluene .....	69.1	0.272	39.6	0.239	1.14
„ .....	311	1.25	124.5	0.751	1.66
„ .....	504	1.99	173	1.04	1.91
<i>o</i> -Nitroanisole .....	76.2	0.301	50.2	0.302	1.0
Nitromethane .....	59.8	0.236	41.4	0.249	0.95
„ .....	121.5	0.479	81.5	0.491	0.98
„ .....	261	1.03	167	1.01	1.02
„ .....	426	1.68	254.5	1.53	1.10
Nitropentane .....	202	0.796	96.7	0.583	1.36
Trichloronitromethane	66	0.26	7.5	0.04	

*Composition of Solutions saturated with Iodine.*

Solvent.	Iodine concentration.		Potassium iodide concentration.		Molecular Ratio $I_2/KI$ .
	Grams.	Gram-mols.	Grams.	Gram-mols.	
<i>o</i> -Nitrotoluene .....	293	1.155	46.1	0.278	4.1
„ .....	517	2.04	86.8	0.523	3.9
„ .....	878	3.46	148	0.891	3.9
<i>m</i> -Nitrotoluene .....	522	2.06	84.2	0.508	4.0
„ .....	758	2.99	123	0.742	4.0
<i>o</i> -Nitroanisole .....	355	1.40	59.8	0.360	3.9
Nitromethane .....	353	1.39	90.0	0.542	2.6
„ .....	657	2.59	157	0.945	2.7
„ .....	944	3.72	211.5	1.275	2.9
Nitropentane .....	943	3.72	176	1.06	3.5

Exactly similar relationships are observable on comparing the experimental data for the three aromatic nitro-compounds now investigated with the results previously obtained for nitrobenzene. For solutions saturated with potassium iodide, the molecular ratio  $I_2/KI$  increases rapidly with increasing concentration, and on this account no definite conclusions can be drawn with regard to the components of the solution. The observations accord, however, with the view that increasing concentration favours the formation of periodides of greater complexity. From solubility measurements alone, the presence of any particular iodide and its concentration in any one of these saturated solutions cannot be determined, but it is probable that with gradually increasing concentration the equilibrium changes are such that the tri-iodide, penta-iodide, hepta-iodide, and enneaiodide in turn become the predominant components of the solution.

Solutions saturated with iodine, on the other hand, all contain approximately four molecules of iodine for each molecule of iodide. In *o*- and *m*-nitrotoluenes and in *o*-nitroanisole, as in nitrobenzene, conditions favourable for the formation of the highest periodide lead therefore to the production of the enneaiodide,  $KI_9$ , the existence of which in solution is clearly characterised by the constancy of the molecular ratio  $I_2/KI = 4$  over a large range of concentrations.

The data obtained for nitromethane differ considerably from those for the aromatic solvents. The difference in behaviour is very clearly seen by a graphic representation of the experimental results. Nitromethane solutions saturated with potassium iodide contain approximately one molecule for each molecule of iodine, and although the molecular ratio  $I_2/KI$  increases with increasing concentration, yet the alteration is much smaller than in the case of the

aromatic nitro-compounds. Furthermore, solutions saturated with iodine do not contain four molecules for each molecule of iodide; for the range of concentrations investigated, the molecular ratio slowly increases with the concentration from 2.5—3. There is therefore little evidence of the existence of the highest periodide,  $\text{KI}_9$ , in the nitromethane solutions under conditions comparable with those where it appears to be the principal component in the aromatic nitro-compounds.

The solubility data for nitropentane are insufficient to justify any very definite conclusions, yet the two experiments carried out indicate that by substituting the amyl for the methyl group, the solubility relationships approximate to those observed for the benzene derivatives and therefore in all probability the nature of the predominant dissolved periodide at any given concentration is the same. Periodides are not formed in trichloronitromethane, the solubility of potassium iodide in presence of iodine being very small.

The solid nitro-compounds were examined either by dissolving them in an inactive solvent and studying the behaviour of the resulting solution towards iodine, or by investigating the solvent capacity of their solutions in nitrobenzene. Of the two methods, the former is *a priori* to be preferred, for with an active nitro-derivative dissolved in an inert solvent the experimental data should give a more or less direct expression of the behaviour of the active constituent. In the second method, the influence of the solid nitro-compound can only be deduced by taking into account the solvent capacity of the admixed nitrobenzene. As will be seen later, this process alone can be applied in the case of the majority of the nitro-compounds investigated.

In order to carry out the further investigation in the manner indicated, a preliminary inquiry into the way in which the solvent capacity of nitrobenzene is altered by admixture with other liquids was necessary. The substances employed for this purpose were carbon tetrachloride, carbon disulphide, chloroform, benzene, toluene, *p*-chlorotoluene, ethyl alcohol, ethyl acetate, and methyl alcohol. Nitrobenzene was mixed with each of these in equal volumes (10 c.c. of each), and the mixed solvents thus obtained were shaken for several hours with iodine and excess of potassium iodide. The experiments were carried out in such a way that the concentration of the iodine in the resulting solutions was in every case approximately the same, and each solution was saturated with potassium iodide. In the following table, the liquid mixed with the nitrobenzene is indicated in the first column, the iodine concentration is given in the second and third columns, and the quantities of dissolved potassium iodide are tabulated in the fourth and fifth columns.

	Iodine concentration		Potassium iodide concentration	
	Grams.	Gram-mol.	Grams.	Gram-mol.
		per litre.		per litre.
Pure nitrobenzene .....	144.3	0.569	80.4	0.484
Carbon tetrachloride .....	144.2	0.568	51.4	0.310
Carbon disulphide .....	144.3	0.569	51.4	0.310
Chloroform .....	145.5	0.573	53.5	0.322
Benzene .....	144.6	0.570	53.6	0.323
Toluene .....	144.5	0.570	51.7	0.312
<i>p</i> -Chlorotoluene .....	144.8	0.571	52.9	0.319
Ethyl alcohol .....	141.2	0.556	93.9	0.565
Ethyl acetate .....	141.8	0.559	93.9	0.565
Methyl alcohol .....	143.1	0.564	123.8	0.946

A glance at the experimental data shows that the effect of mixing the nitrobenzene with an equal volume of carbon tetrachloride, carbon disulphide, chloroform, benzene, toluene, or *p*-chlorotoluene is in every case the same. The amount of potassium iodide which the mixed solvent can take up for one and the same amount of iodine is constant within the limits of experimental error. These admixed substances, therefore, simply dilute the nitrobenzene, and the solvent capacity of the latter is not in any way affected by the specific character of the inert liquid. This result is of some interest in view of the different densities of the liquids, which vary from 0.90 in the case of benzene to 1.63 for carbon tetrachloride. The relative proportions by weight of benzene and carbon tetrachloride added to the same weight of nitrobenzene in the above experiments are as 10 : 18, and yet these very different quantities by weight (representing, however, equal volumes) have the same effect. These results lead to the conclusion that in the investigation of the problem in hand the proportions by volume, and not by weight, must be made the basis of comparison. The conclusion drawn has probably a general significance, and may prove of considerable service in similar investigations. That the foregoing six liquids merely act as diluents is in accord with the fact that none of them takes up potassium iodide, even in presence of large quantities of iodine.

Mixtures of nitrobenzene with ethyl alcohol, ethyl acetate, and methyl alcohol dissolve more potassium iodide than pure nitrobenzene. This is due to the fact that these liquids themselves dissolve considerable quantities of potassium iodide and still larger amounts in the presence of iodine, and hence these are also to be regarded as solvents which promote the formation and solution of periodides.

In the previous experiments, the volumes of the two component

liquids were in every case equal. To obtain further data for the purpose of elucidating the behaviour of solid nitro-compounds towards iodine and potassium iodide, the effect of mixing one and the same quantity of nitrobenzene with different quantities of an inert substance has been determined. Of the inactive liquids, carbon tetrachloride and benzene were chosen for this purpose, and as might almost be expected from the preceding results, the effects produced by these two diluents at corresponding concentrations (volume proportions) are the same. In the table, the proportions by volume (before mixing) are given in the first column, and opposite are numbers representing the iodine and potassium iodide concentrations, all the solutions, as before, being saturated with iodide, and having approximately the same iodine concentration. The last column gives the potassium iodide concentration reduced to a uniform iodine concentration of 144 grams per litre.

Composition of solvent.				Iodine concentration.		KI concentration.		KI concentration (reduced).
				Gram-mols. per litre.		Gram-mols. per litre.		Grams per litre.
$C_6H_5NO_2$ .				Grams.		Grams.		
100	per cent.			144.3	0.569	80.4	0.484	80.3
80	„	20	per cent. $CCl_4$	142.2	0.561	68.9	0.415	69.7
67	„	33	„ „	143.4	0.565	60.8	0.366	61.1
67	„	33	„ $C_6H_6$	143.8	0.567	60.8	0.366	60.9
50	„	50	„ $CCl_4$	144.2	0.568	51.4	0.310	51.3
50	„	50	„ $C_6H_6$	144.6	0.570	53.6	0.323	53.3
33	„	67	„ $CCl_4$	143.9	0.567	44.3	0.267	44.3
33	„	67	„ $C_6H_6$	144.4	0.569	43.2	0.260	43.1
15	„	85	„ $CCl_4$	9.3	0.075	—	—	—

If the numbers in the last column are represented graphically, it is found that the decrease in the amount of potassium iodide dissolved is almost exactly proportional to the increase in the proportion of the carbon tetrachloride or benzene in the mixture.

This relationship holds, at any rate, for solvents ranging from pure nitrobenzene on the one hand to a mixture containing more than 60 per cent. of the inactive component on the other. When the relative proportion of the nitrobenzene is further decreased, precipitation of the nitro-compound from solution takes place, and, as is evident from the last experiment recorded in the table, the quantities of iodine and potassium iodide in the resulting solution are very small. A similar phenomenon has been observed on shaking benzene solutions of several other nitro-compounds with iodine and potassium iodide, and on this

account it has not been possible to employ the first method of investigation suggested on p. 224.

From the data in the previous tables, the amount of potassium iodide dissolved by nitrobenzene when mixed with any given volume proportion of an inactive substance can be directly ascertained for a concentration of iodine of 144 grams per litre. If the amount of iodide dissolved when the inert substance is replaced by an equal volume of some other nitro-compound is greater than this, it would appear justifiable to conclude that this nitro-compound is not inert, but promotes the formation and solution of periodides. In the following table are given the experimental data relating to the solubility of potassium iodide in mixtures of nitrobenzene with other aromatic nitro-compounds, the iodine concentration being in all cases approximately the same. The first three columns give respectively the volume composition of the mixed solvent, the iodine and iodide concentrations; in the fourth, the potassium iodide concentrations are reduced to a uniform iodine concentration (144 grams per litre), and in the fifth column the corresponding numbers which would be obtained for the solubility of the iodide if the nitrobenzene were mixed with the same volume proportion of an inert substance. The figures in the last column are obtained by interpolation from the data in the previous table.

Composition of solvent.			KI concentration from curve for nitrobenzene		
100 per cent.	nitrobenzene	Iodine concentration.	KI concentration.	KI concentration reduced.	+ inactive substance.
100	per cent. nitrobenzene	144.3	80.4	80.2	—
66	„ nitrobenzene	143.2	74.6	75.0	61
34	„ <i>o</i> -chloronitrobenzene				
67	„ nitrobenzene	139.8	75.4	77.5	62
33	„ $\alpha$ -nitronaphthalene				
77	„ nitrobenzene	142.5	78.8	79.5	67
23	„ <i>m</i> -dinitrobenzene				
77	„ nitrobenzene	139.5	76.8	79.1	67
23	„ 2 : 4-dinitrotoluene				
67	„ nitrobenzene	143.5	79.5	79.8	62
33	„ 2 : 4 : 6-trinitrotoluene				
76	„ nitrobenzene	141.9	59.8	60.8	67
24	„ <i>p</i> -nitrobenzyl chloride				

A comparison of the numbers in the last two columns shows that

the solubility of potassium iodide in nitrobenzene when this is mixed with *o*-chloronitrobenzene,  $\alpha$ -nitronaphthalene, *m*-dinitrobenzene, di- or tri-nitrotoluene is considerably greater than when the nitrobenzene is mixed in the same volume proportion with an inactive substance such as benzene or carbon tetrachloride. The solubility numbers in the fourth column for the mixed solvents approximate, indeed, closely to that found for nitrobenzene itself, and the conclusion may be drawn that the above-mentioned nitro-compounds act very similarly to nitrobenzene with regard to the formation of periodides. This appears to be the case whether one or several nitro-groups are present in the molecule, for, according to the table, *m*-dinitrobenzene, 2:4-dinitrotoluene, and 2:4:6-trinitrotoluene agree almost completely with nitrobenzene. The solubility number obtained for the mixture of *o*-chloronitrobenzene and nitrobenzene is undoubtedly somewhat lower than that for pure nitrobenzene and the value found for the mixture of nitrobenzene and *p*-nitrobenzyl chloride is quite different from that obtained in the other cases investigated, and no adequate explanation of the fact is evident.

The composite solutions, the nature of which has been discussed, are characterised by the same iodine concentration and saturation with regard to potassium iodide. It is important to remember, however, that in the case of the liquid aromatic nitro-solvents investigated, the solutions saturated with iodine are much more definitely characterised. Over a considerable range of concentration, the molecular ratio  $I_2/KI$  in these solutions is equal to four, and it was thought possible that the examination of the composition of such solutions, when mixed solvents are used, might give more definite information with regard to the behaviour of those (solid) substances not available for direct investigation. Preliminary experiments with solvents composed of nitrobenzene and an inactive substance showed, however, that the amount of iodine dissolved per molecule of potassium iodide is practically the same as in the case of pure nitrobenzene. In these experiments, carbon tetrachloride was used on account of its small solvent power for iodine (one litre dissolves about 1/10 gram-molecule).

The following numbers show this sufficiently:

Composition of solvent.	Iodine concentration.	KI concentration.	Mol. ratio $I_2/KI$ .
33 per cent. $C_6H_5 \cdot NO_2$ , 67 per cent. $CCl_4$	1.10 gr.-mols.	0.268 gr.-mols.	4.1
67 „ $C_6H_5 \cdot NO_2$ , 33 „ $CCl_4$	1.83 „	0.447 „	4.1

Since the admixed inert liquid exerts apparently no appreciable influence on the proportion of dissolved iodine, the free nitrobenzene, and the mixture of this with nearly 70 per cent. of inert carbon tetrachloride both giving the value 4 for the molecular ratio, it is evident that the examination of such solutions saturated with iodine

and containing nitrobenzene as one component cannot furnish much information with regard to the behaviour of other nitro-compounds.

A consideration of the experimental data obtained for the solubility of the iodide leads, however, to the conclusion that to this extent many aromatic nitro-compounds resemble nitrobenzene in their behaviour towards iodine and potassium iodide. It is by no means possible to ascribe a specific action to the nitro-group, for the formation of periodides of the types which have been discussed probably also takes place in many other solvents.

Of the liquids which have been examined, hexane, benzene, toluene, methyl iodide, chloroform, bromoform, carbon tetrachloride, carbon disulphide, ethyl iodide, bromobenzene, *p*-chlorotoluene, benzyl chloride, and ethyl ether do not dissolve potassium iodide to any appreciable extent in the presence of iodine. These organic liquids do not promote the formation of soluble periodides.

Ethyl alcohol, ethyl cyanide and ethyl acetate, on the other hand, give solutions which certainly contain periodides, but the interpretation of experimental data is in these cases attended with considerable difficulty, for potassium iodide itself is appreciably soluble in the first and the third, and in all three the solubility of iodine is far greater than in the aromatic nitro-compounds which have been investigated. In two other solvents investigated, namely, ethyl bromide and *isobutyl* alcohol, potassium iodide is almost insoluble and its ready solubility in these solvents in presence of iodine is indicative of periodide formation. The quantitative relationships in these two cases differ considerably from those found for ethyl alcohol, ethyl cyanide, and ethyl acetate, as is evident from the following table containing solubility data. The simple solubility of potassium iodide or of iodine in the various solvents is indicated in the second column of the table. The numbers in brackets in the last column of the first part of the table give the molecular ratio  $I_2/KI$  after subtracting the solubility value for potassium iodide from the total iodide concentration.

*Composition of Solutions Saturated with Potassium Iodide.*

Solvent.	Solubility of KI in grams per litre.	Iodine concentration.		KI concentration.		Mol. ratio $I_2/KI$ .
		Grams.	Gram-mols. per litre.	Grams.	Gram-mols. per litre.	
Ethyl alcohol	14.4	96.4	0.38	68.6	0.413	0.92 (1.16)
Ethyl cyanide	4	94.5	0.372	65.1	0.392	0.96 (1.01)
Ethyl acetate	12.8	97.9	0.386	65.8	0.396	0.98 (1.21)
Ethyl bromide	0	100	0.394	18.8	0.113	3.5
<i>isoButyl</i> alcohol	0	96.1	0.379	52.6	0.317	1.2

*Composition of Solutions saturated with Iodine*

Solvent.	Solubility of iodine in grams per litre.	Iodine concentration.		KI concentration.		Mol. ratio- I <sub>2</sub> /KI.
		Grams.	Gram-mols. per litre.	Grams.	Gram-mols. per litre.	
Ethyl alcohol	224	627	2.47	110	0.66	3.75
Ethyl cyanide	110	640	2.52	107	0.645	3.9
Ethyl acetate	141	801	3.16	134	0.81	3.9
Ethyl bromide	211	619	2.44	76.2	0.46	5.3
isoButyl alcohol	78	436	1.22	58.6	0.353	3.5

In the first series of saturated solutions, the iodine concentration is approximately the same in every case; in the second series, the potassium iodide concentrations are not so nearly equal, but the concentrations are such as to make it possible to compare the solutions with the corresponding solutions in aromatic nitro-compounds for which the existence of a simple molecular relationship between iodine and iodide has been experimentally established. The values of the molecular ratio in the ethyl alcohol, ethyl cyanide and ethyl acetate solutions approximate to those found in the case of the aromatic nitro-compounds. It is, however, not justifiable to conclude from this that the periodides present are the same, for the conditions which hold for the solutions in aromatic nitro-compounds, namely, small individual solubilities of iodine and potassium iodide, do not obtain in the last-mentioned solvents. The data in the last table can at the most be regarded as of an orientating character, for in order to compare satisfactorily the properties of these solvents with the nitro-compounds, a series of solubility determinations would be necessary in each case.

Some of the materials employed in this investigation have been purchased with the aid of a grant from the Research Fund of the Royal Society, and the author is much indebted to the Grants Committee for the assistance thus received.

THE YORKSHIRE COLLEGE,  
LEEDS.

# ANNUAL GENERAL MEETING,

MARCH 23RD, 1904.

Professor W. A. TILDEN, D.Sc., F.R.S., in the Chair.

THE PRESIDENT declared the ballot open for the election of Officers and Council for the ensuing year, Mr. G. BARGER and Dr. S. B. SCHRYVER being appointed Scrutators. He then presented the following Report on the state of the Society during the past twelve months :

## REPORT OF THE COUNCIL.

The Council are in the fortunate position of being able to report that the Society continues to increase and flourish. At the date of the Annual General Meeting last year, the number of Fellows was 2,631\* ; since that date, 170 Fellows have been elected and three reinstated, making a gross total of 2,804. Of these, 23 have been removed for non-payment of subscriptions, and the elections of 2 have become void, 28 have resigned, and 17 have died, leaving a net total of 2,734 Fellows on our list.

The names of the Fellows who have died are :

H. G. Adshead.	T. H. Dodd.	C. James.
J. O. Alexander.	T. W. Fletcher.	T. A. Lawson.
A. E. Barrows.	W. Francis.	J. Mactear.
Baron de Bush.	H. B. Fulton.	J. Reddrop.
Samuel Clift.	A. G. Hendry.	G. H. Robertson.
W. H. Corfield.	T. Isherwood.	

The following Fellows have withdrawn :

W. H. Barlow.	W. Grafton.	W. Round.
W. M. Brothers.	A. Hill.	W. J. C. Scrutton.
R. J. Brown.	T. Lemmey.	G. A. Shaw.
A. Collenette.	W. Lewins.	E. A. Smith.
W. Diamond.	H. Macan.	G. C. Thomson.
J. R. Don.	A. M. Martin.	A. L. Thornton.
D. Ferrier.	J. A. Mathews.	G. A. Waterhouse.
A. E. Garrod.	J. Morison.	W. J. Williams.
W. Goodall.	A. A. Ramsay.	A. W. Winterton.
	J. Robson.	

\* Last year this number was incorrectly stated to be 2,471 (*Proc.*, 1903, 19, 81 ; *TRANS.*, 1903, 83, 629).

As in future Reports the accounts and other statistics of the Society will be given for the calendar year, the following data for the year 1903 may be of interest for purposes of comparison. The number of Fellows on January 1st, 1903, was 2,607, and during the year 173 Fellows have been elected and 5 reinstated by the Council, making a gross total of 2,785. Of these, the Society has lost 16 by death, 46 from resignations, and 23 by removal for non-payment of subscriptions, giving the number of Fellows in the Society on December 31st, 1903, as 2,700.

The Society has to lament the death of a distinguished Foreign Fellow, Professor Wladimir Markownikoff, on February 11th, 1904.

The small number of Fellows still living, who were elected in the early days of the Society has been further reduced by the death of Dr. William Francis.

The scientific work of the Society during the past session gives evidence of continued activity. Since the last Annual General Meeting, 163 scientific communications have been made to the Society, 107 of which have already been published in the *Transactions*, and abstracts of all have appeared in the *Proceedings*.

During 1903, 181 scientific communications were made to the Society, 110 of which were published in the *Transactions* for that year, abstracts of all appearing in the *Proceedings* for 1903.

The volume of *Transactions* for 1903 contains 142 memoirs occupying 1,490 pages, whilst that for the preceding year contains 160 memoirs occupying 1,604 pages.

The *Journal* for 1903 contains also 3,882 abstracts which may be classified as follows:—

#### Part I.

	Pages.	No. of Abstracts.
Organic Chemistry .....	872	1650

#### Part II.

General and Physical Chemistry .....	471
Inorganic Chemistry .....	443
Mineralogical Chemistry .....	119
Physiological Chemistry.....	391
Chemistry of Vegetable Physiology and Agriculture .....	242
Analytical Chemistry .....	566
	<hr/>
	768
	<hr/>
Total in Parts I. and II. ....	1640
	<hr/>
	3882

In April last, Professor Emil Fischer was invited to give the Faraday Lecture in the autumn, and provisional arrangements were made for its delivery early in the present session. Much to the regret of the Council, continued ill-health has prevented Professor Fischer from fulfilling his intention, and for the present the hope of numbering him among the Faraday Lecturers has had to be abandoned. The Council are glad to be able to announce that Professor Ostwald will deliver the Faraday Lecture on Tuesday, April 19th, in the Lecture Theatre of the Royal Institution, kindly lent by the Managers for the occasion.

The Centenary of the Enunciation of the Atomic Theory by Dalton was celebrated by the Literary and Philosophical Society of Manchester in May last, and in company with Sir Henry Roscoe, Professor Thorpe, and Professor Frankland, Vice-Presidents, Dr. Scott, Secretary, and Sir William Ramsay, Foreign Secretary, the President attended the meeting, and presented an address in the name of the Chemical Society.

The triennial award of the Longstaff Medal to the Fellow of the Society who, in the opinion of the Council, has done the most to promote chemical science by research in the interval since the last presentation was made, on the recommendation of the Research Fund Committee, to Professor W. J. Pope, F.R.S., for his researches on the stereochemistry of compounds of elements other than carbon.

The Fifth International Congress of Applied Chemistry was held in Berlin in June last, and the President attended as the representative of the Society. An invitation to the Congress to hold its next meeting in London, given by the President of the Society of Chemical Industry, was supported by the President, but on a vote being taken Rome was chosen as the place of the meeting in 1905.

The Council welcomed the opportunity of sending a letter of congratulation to their distinguished Foreign Fellow, Professor Mendeléeff, on the occasion of his seventieth birthday, which occurred on February 9th last.

The increase in the use of the Library mentioned in last year's report has been maintained, as 975 books were borrowed from the Library, as against 925 during the previous year. The additions to the Library comprise 115 books, of which 49 were presented, 268 volumes of periodicals, and 48 pamphlets; as against 84 books, 338 volumes of periodicals, and 23 pamphlets last year. The corresponding numbers for the year ending December 31st, 1903, are 991 books borrowed, the additions to the Library being 126 books, of which 51 were presented, 271 volumes of periodicals, and 43 pamphlets.

The changes proposed in last year's report with regard to the Library have now been carried out, and cases have been erected in one

of the rooms in the basement for the storage of the less used books. These cases will accommodate about 3,500 volumes, and so provide room for the growth of the Library for about seven years. An equal number of cases can be added at any future period without cost beyond that of the cases themselves.

Mr. F. W. Clifford was appointed Librarian on July 1st.

The Council regret to have to record the death, on May 10th, of Mr. Josiah Hall, who for twenty-five years had been Collector to the Society, and who retired in 1895 with a pension of £130 a year. It was decided to grant to Mrs. Hall, his widow, an annuity of £30.

The Society has been the fortunate recipient of two handsome busts in bronze of distinguished chemists, that of Liebig (a copy of the one in Munich) having been presented by Dr. Messel, and that of Dalton, which has been modelled from all available sources by Miss Levick, by Professor Thorpe. Two interesting photographs of portraits have also been received, one of Roger Bacon, presented by Mr. Oscar Guttmann, and one of Dr. Wm. Prout, F.R.S., from his son, the Rev. T. J. Prout.

At an extraordinary General Meeting of the Society held on July 2nd, the proposal of the Council to alter Bye-Law I. so that the annual publications of the Society should not be sent to Fellows who are in arrear with their subscriptions was unanimously approved. To give effect to this change in the Bye-Law, the *Journal* is now issued to Fellows on the last day instead of the first day of the month. An extra number of the *Transactions* was issued on December 31st to provide for the publication of papers which would have appeared on January 1st, 1904, under the old arrangement, and now that the change has been made the net result is that Fellows receive the monthly parts of the *Journal* a day earlier than heretofore.

The first part (Authors' Index) of the Collective Index for the decade 1893—1902, promised provisionally for 1904, was issued in January to those Fellows who had made application for it in accordance with the printed notices circulated with the monthly parts of the *Journal* since last July, and it is hoped that the subject index for the same period may be ready before the end of next year. The rapid publication of the Author's Index is due to the untiring energy and devotion of the Indexer, Mrs. Dougal, and has in no way interfered with the issue of the Annual Index at the end of February, which has been customary since she undertook the work involved in its preparation.

The Second Report of the Joint International Committee on Atomic Weights, which now includes Professor Moissan as the representative of France, with its revised table of atomic weights, has been issued to Fellows both in the *Proceedings* and in the *Journal*.

The Council resolved that the rooms of the Society should be closed not later than 10.30 p.m. on those evenings on which meetings are held, and, as very few Fellows were found to use the Library on Saturday afternoon, it was further resolved that it should be closed at 2 p.m. on Saturdays from the beginning of the present year.

Grants amounting in all to £232 have been made during the year from the Research Fund, of which amount £15 has been returned.

The Council desires to record its deep sense of obligation to Dr. Horace T. Brown for the ability and patience with which he has discharged the duties of Treasurer during the past year. Finding on taking office that a complete reorganisation of the method of collecting the contributions of Fellows and of keeping the Accounts of the Society was immediately necessary, he did not shrink from the immense labour involved in establishing a new system and getting it into operation. The nature of the changes which have been made is explained below, and it is obvious that great sacrifices of time and of personal effort were involved in the process. It is, therefore, with the utmost regret that the Council has received from Dr. Brown an intimation that his engagements no longer permit him to retain office.

In March last it was found that certain subscriptions and admission fees of Fellows which had apparently been paid had not been entered in the Books of the Society. An examination of the Books was made by a firm of Chartered Accountants, and on April 22nd, the late Assistant Secretary, who at that time was acting as Librarian and Curator, was dismissed.

The Accountants subsequently reported that an investigation of the Society's Books, carried back to March, 1895, showed that there was an apparent deficiency amounting to £2306.

The late Assistant Secretary, whilst not admitting the accuracy of the amount of the deficiency, has, up to the present, repaid to the Society sums amounting to £250.

Hitherto, it has been customary for the Treasurer to close the Books of the Society a few days before the Annual General Meeting, and to make up the Accounts to a date as near to that of the Annual Meeting as possible. This arrangement has given rise to considerable inconvenience, owing in the first place to the short time allowed to complete the financial statements, and secondly to the impossibility of conforming strictly to that portion of Bye-Law VIII., which requires the Auditors to report to the Council at least one week before the Annual General Meeting. In future, therefore, the Treasurer will present his Accounts at the Annual Meeting made up to December 31st, instead of to some indeterminate day near the end of March, and these Accounts will be drawn up in a somewhat different form from that previously adopted. A statement of the financial

condition of the Society made up for the year ending December 31st last in this modified form accompanies this Report, including a Revenue and Expenditure Account and Balance Sheet, but the Treasurer has considered it advisable on this occasion to include for purposes of comparison another statement made out on exactly the old lines up to March 12th, and it is to this latter statement, which is comparable with the one of last year, that the following remarks apply.

The total income of the Society, from March 22nd, 1903, to March 12th, 1904, was £7276 16s. 5d., whilst the expenditure for the same period was £6060 17s. 4d., showing an excess of income over expenditure of £1215 19s. 1d., against a surplus last year of £817 7s. 1d. The comparison, however, is not a fair one, unless we adjust the figures in the respective years for the arrears of contributions in each case.

Owing to the alteration in July last of Bye-Law I., by which Fellows who are in arrear with their subscriptions do not receive the publications of the Society, the annual contributions, which become due in January, have been paid up more punctually this year than usual. On March 22nd, 1903, the arrears amounted to £2316, whilst on March 12th this year they were £2008, a difference in favour of this year of £308. When this adjustment is made, the surplus of this year becomes £907 19s. 1d. against £817 7s. 1d. last year, a result which may be regarded as highly satisfactory when we take into consideration certain large items of extraordinary expenditure which have been incurred this year, and which will be alluded to later.

The total amount received this year for Admission Fees, Life Compositions, and Subscriptions is £5809 against £4776 last year, a difference in favour of this year of £1033. This, however, includes £250 received on Account of Arrears of Subscriptions from the late Assistant Secretary, and, as already stated, the subscriptions this year are paid up more closely by £308. With these adjustments, the increased income this year from contributions of Fellows is £475, about half of which is due to the unusually large number of Life Composition Fees.

The sale of the Society's publications, and the proceeds of the advertisements in the Journal have brought in £40 9s. 4d. more than last year.

With regard to investments, the Treasurer has to report that since the last General Meeting he has, with the authority of the Council, purchased on behalf of the Society £1500 of Transvaal 3 per cent. Guaranteed Stock. The investments on the General Account now stand at £18,909 0s. 5d., whilst those of the Research Fund Account are valued at £6659 5s. 5d.

The total expenditure this year shows the large increase of

£665 19s. 4*d.*, which is due to certain large items of an exceptional nature.

The balance of the cost of the first volume of the Decennial Index, 1893—1902, amounting to £386 9s. 7*d.*, is chargeable against this year's revenue, being an increase of £254 5s. 3*d.* The completion of the Library Catalogue was announced in the Report of last year, but the main cost of £156 16s. 0*d.* has been borne by the present accounts. The additional accommodation for books referred to in an earlier part of this Report has been provided at a cost of £128 2s. 4*d.* Two other large items of expenditure of an exceptional nature amounting to £228 1s. 6*d.* are included under Accountants' and Legal charges, and are mainly attributable to the special investigation of the Society's Accounts to 1895, to which reference has already been made above.

It is satisfactory to notice that the expenses incidental to the publication of the Journal show a decrease this year of about £100.

The system of keeping the Treasurer's accounts has undergone revision during the past year, the old system having been found insufficient for the present needs of the Society.

At the request of the Council, Messrs. W. B. Keen and Co., Chartered Accountants, have opened up a new set of books, and have also undertaken to give the Treasurer a quarterly audit, and to assist in the preparation of the accounts for the Annual Statement.

This arrangement, which guarantees skilled professional assistance and a thorough checking of the accounts at frequent intervals, has now been in operation for some time, and will not entail any additional expense to the Society, as the appointment of a Treasurer's Assistant is thereby rendered unnecessary.

Arrangements have been made with Messrs. Coutts and Co., the Society's Bankers, by which in future they will receive the contributions of Fellows direct.

## INCOME AND EXPENDITURE ACCOUNT

		<i>Income.</i>			
		£	s. d.	£	s. d.
To Life Compositions ... ..		364	0 0		
„ Admission Fees ... ..		648	0 0		
„ Annual Subscriptions ... ..		4141	0 0		
„ Cash on account of Subscriptions and Fees of past years per Mr. R. Steele ... ..		250	0 0	5403	0 0
„ Investments:—					
Dividends on £6,730 Metropolitan Consolidated 3½ per cent. Stock ...		222	16 0		
£1,050 London and North Western Railway 3 per cent. Debenture Stock ... ..		29	13 4		
£1,520 14s. 3d. Cardiff Corporation 3 per cent. Stock ...		43	3 0		
£1,400 India 2½ per cent. Stock ... ..		33	2 2		
£2,358 Midland Railway 2½ per cent. Preference Stock ...		55	10 3		
£2,400 Bristol Corporation 2½ per cent. Debenture Stock ...		57	5 9		
£1,200 Leeds 3 per cent. Stock ... ..		34	1 0		
Income Tax Recovered ... ..		26	9 0		
Bank Interest on Deposit Account ... ..		17	13 5	519	13 2
„ Publications:—					
Sales:					
Journals ... ..		721	5 6		
Proceedings ... ..		17	15 6		
General Index ... ..		68	8 6		
Memorial Lectures ... ..		23	8 9		
Library Catalogue ... ..		27	5 3		
Jubilee Volume ... ..		1	2 6		
		859	6 0		
Less Publishers' Commission ... ..		76	18 3		
		782	7 9		
Proceeds of Advertisements in Journal ... ..	£82 12 10				
Less Commission ... ..	12 8 2				
		70	4 8	52	12 5
„ Subscriptions from other Societies:—					
Society of Chemical Industry ... ..		9	9 0		
Society of Public Analysts ... ..		10	10 0		
Physical Society ... ..		14	3 6		
Faraday Society ... ..		1	1 0		
District Agricultural Analysts' Association ... ..		0	10 6	35	14 0
„ Sale of Apparatus ... ..				7	0 0

FOR THE YEAR ENDED 31ST DECEMBER, 1903.

*Expenditure.*

	£	s.	d.	£	s.	d.
By Expenses on account of Journal and Proceedings:—						
Salary of Editor ... ..	300	0	0			
Salary of Sub-Editor ... ..	200	0	0			
Salary of Indexer ... ..	80	0	0			
Editorial Postages ... ..	15	12	10			
Abstractors' Fees ... ..	404	5	5			
Printing of Journal ... ..	1922	15	10			
Printing of Advertisements ... ..	29	15	7			
Printing of Wrappers ... ..	112	16	6			
Distribution of Journal ... ..	436	18	6			
Authors' Copies ... ..	94	18	0			
				3597	2	8
Printing of Proceedings ... ..	211	14	2			
Distribution of Proceedings ... ..	46	14	5			
Printing of Bye-Laws... ..	27	5	9			
				285	14	4
„ Collective Index 1893-1902:—						
Salaries ... ..				130	3	3
„ Library Expenses:—						
Salary of Librarian ... ..	112	1	6			
Books and Periodicals ... ..	226	17	7			
Binding ... ..	59	16	8			
Book-Case ... ..	128	2	4			
Library Sundries... ..	9	19	4			
Gratuity to Assistant... ..	10	0	0			
				546	17	5
„ Printing Library Catalogue... ..				156	16	0
„ Indexing for International Catalogue ... ..				30	0	0
„ Bunsen Memorial ... ..				20	0	0
„ Balance of Dinner Account ... ..				19	6	8
„ Illuminated Address to Literary and Philosophical Society, Manchester ... ..				2	12	6
„ Administrative Expenses:—						
Tea Expenses ... ..	26	12	5			
Salary of Assistant Secretary... ..	150	0	0			
Salary of Office Assistant... ..	28	4	0			
Treasurer's Assistant .. ..	5	0	0			
Wages (Commissionaire, Housekeeper, Charwomen) ... ..	163	10	6			
Pension to Mr. Hall ... ..	48	17	8			
Pension to Mrs. Hall... ..	18	14	0			
Gas and Electric Light ... ..	27	14	2			
Coal and Coke ... ..	19	12	0			
Repairs and Cleaning... ..	60	2	0			
Petty House Expenses ... ..	36	8	3			
Gratuities ... ..	3	5	8			
Insurance ... ..	6	9	2			
Guarantee Society ... ..	2	2	6			
Accountants' Charges ... ..	10	10	0			
„ „ Special Investigation, 1896-1902 ... ..	158	5	0			
„ „ Designing and Opening New Books ... ..	25	10	0			
Legal Charges ... ..	44	6	6			
Miscellaneous Printing ... ..	106	3	6			
Stationery ... ..	60	10	7			
Office Furniture ... ..	31	17	2			
Bank Charges ... ..	1	8	10			
Postages... ..	99	3	11			
Sundry Expenses... ..	3	17	7			
				1138	5	5
„ Balance, being Excess of Income over Expenditure carried to Balance Sheet ... ..				891	1	4
				£6817	19	7



FOR THE YEAR ENDED 31ST DECEMBER, 1903.

*Expenditure.*

By Grants to—	£	s.	d.	£	s.	d.
J. B. Cohen .....	5	0	0			
J. McCrae.....	5	0	0			
J. J. Sudborough .....	20	0	0			
R. S. Morrell .....	15	0	0			
J. N. Collie .....	25	0	0			
T. S. Patterson .....	12	0	0			
A. Lapworth .....	15	0	0			
A. W. Harvey .....	10	0	0			
J. Wade .....	10	0	0			
F. Soddy .....	25	0	0			
H. A. Auden .....	5	0	0			
J. C. Cain.....	10	0	0			
F. G. Donnan .....	10	0	0			
G. D. Lander .....	10	0	0			
B. Prentice .....	10	0	0			
A. Slator .....	10	0	0			
S. Smiles .....	10	0	0			
B. D. Steele.....	25	0	0			
				232	0	0
By Longstaff Honorarium, Professor W. J. Pope ..				20	0	0
„ Cost of Longstaff Medal, Professor W. J. Pope				1	10	0
„ Cheque Book .....				0	8	0
				£253	18	0

Society and certify them to be in accordance therewith. I have also verified the

Approved—	LEONARD TEMPLE THORNE.	} Auditors.
	GERALD T. MOODY.	
	JORN WADE.	

## THE TREASURER IN ACCOUNT WITH THE CHEMICAL

Dr.	£	s.	d.	£	s.	d.
Balance at Bank, 21st March, 1903 ... ..	1707	9	1			
„ in hands of Treasurer ... ..	1	2	0			
Transferred from Deposit Account (30th November, 1903) ... ..				1708	11	1
				1000	0	0
Receipts by Life Compositions, Admission Fees and Subscriptions from 21st March, 1903, to 12th March, 1904:—						
Life Compositions ... ..	542	0	0			
Admission Fees ... ..	672	0	0			
Cash on Account of Subscriptions and Fees for past years per Mr. R. Steele ... ..	250	0	0			
Subscriptions in Arrear ... ..	137	0	0			
„ for 1903 ... ..	1413	0	0			
„ „ 1904 ... ..	2793	0	0			
„ „ 1905 ... ..	2	0	0			
				5809	0	0
Sale of Journals ... ..	721	5	6			
„ Proceedings ... ..	17	15	6			
„ General Index ... ..	71	15	6			
„ Memorial Lectures ... ..	22	6	3			
„ Library Catalogue ... ..	8	5	3			
„ Jubilee Volume... ..	1	2	6			
Proceeds of Advertisements in Journal ... ..	86	16	6			
				929	7	0
Subscription from the Society of Chemical Industry ... ..	9	9	0			
„ „ „ Public Analysts ... ..	10	10	0			
„ „ „ Physical Society ... ..	14	3	6			
„ „ „ Faraday Society ... ..	1	1	0			
„ „ „ District Agricultural Analysts' Association ... ..	10	6				
				35	14	0
Year's Dividends on £6,730 Metropolitan Consolidated 3½ per cent. Stock ... ..	223	15	8			
Year's Dividends on £1,050 London and North-Western Railway 3 per cent. Debenture Stock ... ..	29	18	7			
Year's Dividends on £1,520 14s. 3d. Cardiff Corporation 3 per cent. Stock ... ..	43	10	6			
„ „ £1,400 India 2½ per cent. Stock ... ..	33	5	1			
„ „ £2,358 Midland Railway 2½ per cent. Preference Stock... ..	56	0	2			
„ „ £2,400 Bristol Corporation 2½ per cent. Debenture Stock ... ..	57	5	0			
„ „ £1,200 Leeds Corporation 3 per cent. Stock ... ..	34	7	0			
Interest on Bank Deposit ... ..	17	13	5			
				495	15	5
Sale of Apparatus ... ..				7	0	0

<i>Assets.</i>	<i>Estimated Value.</i>
12th March, 1904.	£ s. d.
Balance at Bank (Current Account) ... ..	1452 7 9
„ „ (on Deposit) ... ..	1000 0 0
„ in hands of Treasurer ... ..	11 8 11
£6,730 Metropolitan Consolidated 3½ per cent. Stock ... ..	6904 12 0
£1,050 London and North-Western Railway 3 per cent. Debenture Stock ... ..	987 0 0
£1,520 14s. 3d. Cardiff Corporation 3 per cent. Stock... ..	1345 16 6
£2,358 Midland Railway 2½ per cent. Preference Stock ... ..	1697 15 3
£2,400 Bristol Corporation 2½ per cent. Debenture Stock ... ..	1572 0 0
£1,400 India 2½ per cent. Stock... ..	1106 0 0
£1,200 Leeds Corporation 3 per cent. Stock... ..	1092 0 0
£1,500 Transvaal 3 per cent. Guaranteed Stock... ..	1440 0 0
	<u>£18,909 0 5</u>

The sum of £47 12s. 6d., being claim for return of Income Tax, has not yet been received.

£9985 7 6

I have examined the above account with the Books and Vouchers of the Society, and certify

W. B. KEEN,  
Chartered Accountant.

17th March, 1904.

SOCIETY, FROM 22ND MARCH, 1903, TO 12TH MARCH, 1904.

*Expenses on Account of the Journal and Proceedings.*

CR.

	£	s.	d.	£	s.	d.
Salary of Editor ... ..	300	0	0			
„ Sub-Editor ... ..	290	0	0			
„ Indexer ... ..	80	0	0			
Editorial Postages ... ..	14	10	2			
Abstractors' Fees ... ..	404	5	5			
Printing of Journal ... ..	1866	16	1			
„ Advertisements ... ..	27	12	2			
„ Wrappers ... ..	108	16	6			
Distribution of Journal by Printers ... ..	395	4	10			
„ „ Society ... ..	14	6	8			
Authors' Copies... ..	84	18	0			
				3496	9	10
Printing of Proceedings ... ..	184	17	6			
Distribution of Proceedings ... ..	37	8	5			
				222	5	11
Publisher's Commission ... ..	76	18	3			
Advertising Agent's Commission ... ..	13	0	9			
				£9	19	0

*Expenses on Account of Collective Index.*

Salaries ... ..	133	6	7			
Printing ... ..	237	6	0			
Postage ... ..	15	17	0			
				356	9	7

*Expenses on Account of the Library Catalogue.*

Printing ... ..	156	16	0
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*Expenses on Account of the Library.*

Salary of Librarian... ..	95	8	2			
Books and Periodicals ... ..	232	1	7			
Binding ... ..	59	16	8			
Gratuity to Assistant ... ..	10	0	0			
Book Case ... ..	128	2	4			
Other expenses ... ..	7	3	2			
				532	11	11

*House Expenses.*

Providing Refreshments ... ..	26	2	9			
Lighting the Building ... ..	27	14	2			
Heating the Building ... ..	14	7	0			
Repairs and Cleaning ... ..	61	8	10			
Petty House Expenses ... ..	38	1	2			
Wages (Commissionaire, House Porter, and Charwomen) ... ..	149	9	9			
Gratuities ... ..	3	9	8			
				320	13	4
Salary of Assistant Secretary ... ..				150	0	0
Pension to Mr. Hall ... ..				16	7	8
„ Mrs. Hall ... ..				26	4	0
Office Assistant... ..				35	2	6
Miscellaneous Printing ... ..				95	0	0
Printing Charter and Bye-laws ... ..				18	10	9
Stationery ... ..				49	18	7
Indexing for International Catalogue ... ..				30	0	0
Office Furniture ... ..				32	17	11
Bank Charges ... ..				1	10	9
Postages ... ..				85	11	4
Dinner Account, Balance ... ..				19	6	8
Guarantee Society Premium ... ..				2	2	6
Illuminated Address, Literary and Philosophical Society, Manchester... ..				2	12	6
Insurance (till 1910) ... ..				37	14	0
Bunsen Memorial ... ..				20	0	0
Accountants' Charges, Special Investigation 1896—1902 ... ..				158	5	0
„ „ Designing and Opening New Books ... ..				25	10	0
Solicitor's Charges ... ..				44	6	6
Sundry Expenses ... ..				4	11	1
Amount placed on Deposit ... ..				1000	0	0
Purchase of £1500 Transvaal 3 per cent. Guaranteed Stock ... ..				1460	13	6
Balance at Bank ... ..	1452	7	9			
„ in hands of Treasurer ... ..	11	8	11			
				1463	16	8
				£9985	7	6

It to be in accordance therewith. I have also verified the Bank Balance and the Investments.

Approved

LEONARD TEMPLE THORNE.  
GERALD T. MOODY.  
JOHN WADE.

Auditors.



THE TREASURER OF THE CHEMICAL SOCIETY IN ACCOUNT WITH THE RESEARCH FUND.

DR.

FROM 21ST MARCH, 1903, TO 12TH MARCH, 1904.

CR.

1903 Mar. 22.		£	s.	d.	£	s.	d.
Balance at Bank, 22nd March, 1903 .....					164	3	11
Year's Dividends on £4,400 Metropolitan Consolidated 3½ per cent. Stock .....		146	6	2			
Year's Dividends on £1,000 North British Railway 4 per cent. No. 1 Preference Stock ..		37	14	4			
Year's Dividends on £1,034 Great Western Railway 2½ per cent. Debenture Stock .....		24	11	2			
					208	11	8
Repayment of Unexpended Grants					45	14	1
1904. Mar. 12.	<i>Estimated Value.</i>	£	s.	d.	£	s.	d.
Balance at Bank.....	164	11	8				
£4,400 Metropolitan Consoli- dated 3½ per cent. Stock.....	4488	0	0				
£1,000 North British Railway 4 per cent. No. 1 Preference Stock .....	1195	0	0				
£1,034 Great Western Railway 2½ per cent. Debenture Stock ..	811	13	9				
					£6659	5	5
The sum of £20 2s. 5d., being claim for return of Income Tax, has not yet been received.							
					£418	9	8

I have examined the above Account with the Books and Vouchers of the Society and certify it to be in accordance therewith. I have also verified the Bank Balance and the Investments.

17th March, 1904.

W. B. KEEN,  
*Chartered Accountant.*

W. B. KEEN,

*Chartered Accountant.*

Approved—

LEONARD TEMPLE THORNF.

GERALD T. MOODY.

JOHN WADE.

*Auditors.*

Professor H. B. DIXON moved the adoption of the report, which was seconded by Mr. E. W. VOELCKER and carried unanimously.

Dr. SCOTT proposed, and Dr. PHILIP seconded, a vote of thanks to the Auditors, which was acknowledged by Dr. MOODY.

The PRESIDENT then delivered his address, which will be found on p. 493.

Professor EMERSON REYNOLDS proposed a vote of thanks to the President, coupled with a request that he would allow his address to be printed in the *Transactions*.

Mr. DAVID HOWARD seconded the motion, which was carried by acclamation and acknowledged by the PRESIDENT.

Professor DIVERS proposed a vote of thanks to the Treasurer, Secretaries, and Council. This was seconded by Mr. SPILLER and unanimously adopted. Dr. SCOTT responded.

The Scrutators presented their report to the President, who declared the following to have been duly elected as Officers and Council for the ensuing year :

*President* : W. A. Tilden, D.Sc., F.R.S.

*Vice-Presidents who have filled the office of President* : H. E. Armstrong, Ph.D., LL.D., F.R.S. ; A. Crum Brown, D.Sc., LL.D., F.R.S. ; Sir W. Crookes, F.R.S. ; James Dewar, M.A., LL.D., F.R.S. ; A. Vernon Harcourt, M.A., D.C.L., F.R.S. ; H. Müller, Ph.D., LL.D., F.R.S. ; W. Odling, M.A., M.B., F.R.S. ; W. H. Perkin, Ph.D., LL.D., F.R.S. ; J. Emerson Reynolds, Sc.D., M.D., F.R.S. ; Sir H. E. Roscoe, LL.D., F.R.S. ; W. J. Russell, Ph.D., F.R.S. ; T. E. Thorpe, C.B., LL.D., F.R.S. ; A. W. Williamson, LL.D., F.R.S.

*Vice-Presidents* : Horace T. Brown, LL.D., F.R.S. ; Harold B. Dixon, M.A., F.R.S. ; Wyndham R. Dunstan, M.A., F.R.S. ; P. F. Frankland, LL.D., F.R.S. ; David Howard ; Raphael Meldola, F.R.S.

*Secretaries* : W. P. Wynne, D.Sc., F.R.S. ; M. O. Forster, D.Sc., Ph.D.

*Foreign Secretary* : Sir W. Ramsay, K.C.B., LL.D., F.R.S.

*Treasurer* : Alexander Scott, M.A., D.Sc., F.R.S.

*Other Members of Council* : Augustus E. Dixon, M.D. ; J. J. Dobbie, M.A., D.Sc. ; Bernard Dyer, D.Sc. ; Alfred D. Hall, M.A. ; A. Harden, D.Sc., Ph.D. ; J. T. Hewitt, M.A., D.Sc. ; C. A. Kohn, Ph.D., B.Sc. ; A. Lapworth, D.Sc. ; J. E. Marsh, M.A. ; E. J. Mills, D.Sc., F.R.S. ; S. Ruhemann, M.A., Ph.D. ; J. M. Thomson, LL.D., F.R.S.

The proceedings then terminated.

## PRESIDENTIAL ADDRESS.

Delivered at the ANNUAL GENERAL MEETING, MARCH 23RD, 1904.

By WILLIAM AUGUSTUS TILDEN, D.Sc., F.R.S.

I CANNOT commence the Address which, in accordance with long-established custom, it is my privilege to offer on this occasion without expressing my most grateful thanks to the Society for the honour conferred in raising me to the office of President, and to my colleagues on the Council, and especially to the Secretaries, and to all the Fellows attending the ordinary meetings, for their unvarying kindness during my year of office.

The past year has been comparatively uneventful, but as a period of steady progress it may be regarded with satisfaction. Our numbers and income have increased, our Journal has been produced with unfailing punctuality, a fact which we owe to the care of our Editors, and its contents are fully equal in quality to those of any previous year. The Society has received several interesting gifts, enumerated in the Report of the Council, for which the thanks of the Society have been returned.

In May last, in company with several other officers of the Society, I attended the celebration in Manchester of the Centenary of the Enunciation of the Atomic Theory and presented an address to the Literary and Philosophical Society on behalf of the Chemical Society. On this occasion the Dalton Lecture was given by Professor F. W. Clarke, of Washington, and the meeting was attended by Professor van't Hoff, from Berlin.

In June, together with a considerable number of British chemists, I visited Berlin on the occasion of the Congress of Applied Chemistry, held in that city. Having been appointed by the Government to represent the Board of Education, and as the representative of the Chemical Society, I was elected a Vice-President of the Congress, and at the inaugural general meeting in the presence of H. R. H. Prince Friedrich Heinrich of Prussia, at the request of the English-speaking delegates, I gave a short address of congratulation. Later I seconded the resolution proposed by the President of the Society of Chemical Industry that the next Session of the Congress be held in London. That resolution was very warmly supported by many of the German members, although it was ultimately lost by a small majority in favour of Rome.

Happily death has been less busy among the more distinguished of our Fellows than has been the case for several years. We have to

mourn the loss of only one of our Foreign Members, Professor W. Markownikoff, of Moscow, who passed away on Feb. 11th, full of years and honours. The volume of Transactions for 1903 is distinguished from the volumes for many preceding years in containing no memorial lecture.

One of my predecessors in this Chair, in an address distinguished alike by intrinsic interest and charm of style, has given the history of the development of scientific chemistry in Great Britain from the beginning of the nineteenth century to the foundation of our Society. It is to be regretted that he did not find an opportunity for completing this survey of English chemistry by carrying the story on through the sixty years which have elapsed since that time. Although the history of the development of the Society has been embodied in the interesting contributions to the Jubilee volume which we owe to Professor Warington and Professor Armstrong respectively, it occurred to me that a review of the state of knowledge and of theory in chemistry during the early years of the Society and the influence of the Society on the progress of scientific chemistry in this country would be useful.

I confess that I often look back with mingled interest and curiosity to the time, now forty years ago, when Hofmann was President and Odling a very active Secretary.

The first meeting of the Society I ever attended was toward the end of 1862, in one of the small rooms on the ground floor of old Burlington House, and the first event I distinctly remember was the lecture by Berthelot on "Synthetic Methods in Organic Chemistry," which was given on June 4th, 1863. As a frequent attendant at the meetings of the Society since that distant day, I am in the position of a spectator who, during two-thirds of the life of the Society, has been a witness of the successive changes of language, of subjects, and of ideas involved in the various contributions to its proceedings.

The establishment of the Journal in 1841 could not fail to supply a stimulus to the prosecution of research, and the three volumes of "Memoirs of the Chemical Society" contain many papers of importance, including contributions from eminent foreign chemists. In the second annual report the Council state that "it is now sufficiently evident that ample materials exist in England for a Chemical Society." The second volume of Memoirs (1843-5) justifies this remark; at the same time the activity of the Giessen laboratory is made manifest in the contributions received from "Dr. August Wilhelm Hofmann, Assistant in the Giessen Laboratory," and from "Alexander W. Williamson, Esq." who acknowledges "the presence and counsel of Professor Liebig."

At the anniversary Meeting in 1847, however, the report of the

Council contains the following interesting passage: "Although an event not immediately connected with the Society, the Council has much pleasure in commemorating the late successful establishment in London of Chemical Laboratories expressly designed to further the prosecution of original research. The new laboratories of the College of Chemistry, and of the two older Colleges of the London University, now offer facilities for practical instruction and research not surpassed, we believe, in any foreign school. They already exhibit their efficiency and claim our grateful recognition in the persons of new and promising contributors to our Memoirs."

The anticipations here expressed were not to be disappointed, for in the succeeding years the pages of the Quarterly Journal then issued by the Society were constantly enriched with the results of researches chiefly from the College of Chemistry, including the famous work of Mansfield on Coal Tar (Oct., 1848), and the researches of Hofmann on the Volatile Organic Bases (April, 1848, *et seq.*). It is also interesting to those who remember our former able Editor, Henry Watts, to notice that the first contributions from the Birkbeck Laboratory, University College, were supplied by him.

During the early years of the existence of the Society the friendly co-operation of eminent foreign chemists is noticeable, and the names of Liebig, Redtenbacher, Bunsen, Fresenius, Schoenbein, Will, and Wöhler appear among the direct contributors to the pages of the Memoirs. With the increase in the number of members, a proportionate increase in the amount of research in pure chemistry does not appear to have been accomplished, and as time went on the number of papers directly contributed to the Journal was comparatively small. Taking a volume at random of the Quarterly Journal we find from the report of the Council a list of only eighteen papers read between March 30, 1855, and March 31, 1856. Seven discourses, however, were given in the same period.

In 1862 the quarterly issue was replaced by a monthly issue, and the number of papers rose to thirty-five, with three discourses. This activity was, however, not long maintained. The thin volumes of the new series contain a good many reprints from the *Philosophical Transactions* and the *Proceedings of the British Association* and other bodies, and not until some twenty years later was this number of papers approximately doubled, although the numerical strength of the Society had in the meantime risen from 360 (1862) to 1,034 (1880).

The number of communications to the Society is, however, not a full and true measure of the assistance which it affords to the progress of science. The opportunities for personal interchange of views among those Fellows who attend the meetings form one of the most

potent influences in helping the development of ideas, and the discussions, often more animated forty years ago than at present, did much at that time to crystallise the amorphous ideas floating in the minds of chemists. Unfortunately, the greater part of the discussions which were carried on at the meetings of the Society are irrecoverably lost.

An examination of the early volumes issued by the Chemical Society gives a clue to the problems which occupied attention in 1841 and onward.

The most notable contribution to Part I. of the Memoirs is a paper "On the Atomic Weight of Carbon," by Professors Redtenbacher of Prague, and Liebig of Giessen. The method used by these investigators did not lead to results of great accuracy, but their work reminds us of the enormous amount of skill and labour which was at this period absorbed in the endeavour to determine with precision the combining proportions of the chief elements. In 1842, Dumas published his work on the ratio of H to O in water, and about the same time Penny, Pelouze, and Marignac were working on the combining weight of chlorine. The labours of Berzelius in the same field were over, and those of Stas belong to a later time.

Part II. of the Memoirs is equally reminiscent, containing the paper "On the Radical of the Cacodyl Series of Compounds," by Professor Bunsen of Marburg. With reference to the discovery of cacodyl, the author elsewhere remarks (*B.A. Report*, July, 1841) that "the theory of compound radicals has received a confirmation scarcely to be gainsaid; for not only has the radical itself been insulated, but the whole cacodyl series has been formed from it directly."

The word "radical" has at different times received different applications, but at the time now referred to it had assumed a well-recognised connotation arising out of the discoveries of Liebig and Wöhler, then fresh in the minds of chemists. After the recognition of benzoyl in the bitter almond series, many investigations were directed toward the isolation of these quasi-elemental components of organic compounds, and one of the most famous of such attempts is embodied under the title, "The Isolation of the Organic Radicals," by E. Frankland, in the *Quarterly Journal of the Society* for 1850.

In 1841, Berzelius was still living, and his authority was predominant in respect to ideas of constitution, and it was not until many years later that the views expressed by Laurent and Gerhardt, the synthesis of organic bases by Wurtz and Hofmann, the discovery of the organo-metallic compounds by Frankland, the introduction of the water type by Williamson successively and conjointly shaped the course of chemical theory toward the ideas which have prevailed in the latter half of the Society's history.

The pages of the Journal from 1841 onwards give, however, little evidence of the process of change. One of the first references to the views of Laurent and Gerhardt is contained in a paper by Hofmann in the Quarterly Journal for July, 1850, in which the notion is brought forward that "the bodies described under the names of methyl and ethyl might with more probability be considered as homologues of marsh gas." The same view was discussed a few months later by Brodie, who proposed for the first time the constitution which we have now so long been accustomed to attribute to the molecule of hydrogen, and which is expressed by the formula  $H_2$ . The arguments used by Brodie were based on the views he had recently put forward, which involved the notion of polarity in the two assumed components of the elementary molecule. In a paper by Kolbe (1851) "On the Constitution and Nature of Organic Radicals," it is remarked that the principal support for the view extensively entertained that methyl, ethyl, butyl, amyl, and capryl in the isolated state possess double the atomic weight assigned to them, that therefore their composition should be expressed by the empirical formulæ  $C_4H_6$  (methyl), &c. . . is found in the circumstance to which attention was first called by Hofmann that the boiling points of butyl, amyl, and capryl differ from each other successively by  $40^\circ$ , on account of the difference in their composition of  $2C_2H_2$ , while if they were composed according to the formulæ  $C_8H_9$ ,  $C_{10}H_{11}$ ,  $C_{12}H_{13}$ , their boiling points would only differ successively by  $20^\circ$ ."

The same volume of the Quarterly Journal (1851) contains the famous paper by Williamson, "On Etherification," as well as a reprint of a characteristic paper from the same hand, "On the Constitution of Salts." The latter contains an exposition of the doctrine of types, an idea originally due to Dumas, but newly conceived by the author, in which his view is clearly distinguished from that of Gerhardt, whose types were never put forward except as synoptic formulæ for the purposes of classification. Williamson, however, declared his opinion that a name should be made to represent what we conceive a compound *to be*, and his formulæ were "used as an actual image of what we rationally suppose to be the arrangement of constituent atoms in a compound, as an orrery is an image of what we conclude to be the arrangement of our planetary system." It was, however, a good many years before views of this kind obtained general acceptance.

In 1852, Frankland announced the principle of "atomicity," and stated clearly for the first time that the combining capacity of each atom is definite and usually limited. About the same time, Gerhardt pointed out the necessity for choosing a unit for molecular magnitudes and for the construction of formulæ. For this purpose, he applied practically the generalisation put forth half a century earlier by

Avogadro, but up to this time neglected. How far the chemists of that day were from recognising all the consequences of assigning to the atoms of elements a definite capacity of combination is illustrated by the distinction maintained between marsh gas and methyl hydride, between methyl and ethyl hydride which were supposed, even by Frankland himself, to be isomeric and not identical, a distinction only partly cleared away in 1862—1863 by Schorlemmer (*Journ. Chem. Soc.*, 15, 419, 16, N.S. 1, 216, 425).

The years 1853—1854 were distinguished by the activity with which the views of Gerhardt and of Williamson were discussed, while the transition from binary formulæ to the unitary system and to ideas of constitution was slowly proceeding.

The *QUARTERLY JOURNAL* for 1855 contains a paper by "William Odling, M.B., F.C.S., Lecturer on Natural Philosophy and Demonstrator of Chemistry at Guy's Hospital" on the constitution of acids and salts, in which the dashes to which we have been so long accustomed were introduced for the first time to indicate the different substitution values of simple and compound "atoms." Further on in the same volume is to be found Dr. Kolbe's "Critical Observations on Williamson's Theory of Water, Ethers, and Acids," and the masterly and crushing rejoinder thereto by Williamson.

Other indications of the fermentation in chemical theory proceeding at this period are afforded by the subjects of the discourses delivered before the Society, of which two very notable examples occur in the volume for 1859. The first is on "The Atomic Weights of Oxygen and Water," by Odling, then one of the Secretaries; the second "On Ammonia and its Derivatives," by Hofmann.

From the former, one or two short extracts may be usefully taken to show what questions still remained unsettled, but the whole paper deserves to be read, by teachers especially, at the present day, affording as it does a perfect model of masterly reasoning and dexterous marshalling of facts. "Whether an atom of water contains the same quantity or double the quantity of hydrogen that is contained in an atom of hydrochloric acid, and whether the atomic weight of oxygen is 8 or 16, are concrete examples of the many disputed questions which lie at the very basis of scientific chemistry . . . . Apart from the absolute accuracy or falsity of any explanation, it is evidently most inconsequent to interpret, as many chemists do, a certain set of facts in one special manner and a precisely similar set of facts in an opposite manner . . . . The majority of English chemists represent the atomic weight of carbon by 6, that of oxygen by 8, and that of sulphur by 16. Dr. Frankland would double the atomic weight of carbon, but would retain the old atomic weights of oxygen and sulphur. Mr. Griffin, who lays claim to priority in doubling the

atomic weights of carbon and oxygen, ridicules the notion of doubling that of sulphur. Dr. Williamson, Mr. Brodie, and myself have for a long time past advocated the doubling of all three."

Hofmann's discourse is interesting as showing the fascination which the doctrine of types exercised over certain minds, arising doubtless from the facilities it afforded for bringing into order the rapidly increasing number of new substances which continued to pour forth from the laboratory. But of course its indiscriminate application led to many erroneous ideas.

How slowly new views are assimilated in such a branch of science as chemistry, influenced as it has so long been by the sort of formulæ which successively happened to be fashionable, is shown by the fact that the idea of limited valency put forward by Frankland in 1852 required further exposition in 1860, when he gave to the Chemical Society a discourse on "Organo-Metallic Bodies" (Quarterly Journal, 13, 177). The idea of polyatomic (multivalent) radicles had been introduced long before, in 1851, by Williamson in the paper already quoted (Quarterly Journal, 4, 350), but notwithstanding the accumulation of facts, the application of the idea was far from being generally adopted till much later. I distinctly remember the inconvenience to students during the period of transition, and when, in 1861, I attended some of Hofmann's lectures, the change of  $O=8$  to  $O=16$  and  $C=6$  to  $C=12$ , together with the transformation of  $KOCO_2$  into  $K_2CO_3$  occurred in the middle of the course, much to the dismay of beginners like myself.

The new volume of the monthly Journal for 1862 contains a beautiful discourse by Wurtz, "On Oxide of Ethylene considered as a Link between Organic and Mineral Chemistry," in which comparing with oxide of ethylene, the oxides of barium, and other metals, he urged the duplication of the atomic weights of these elements. He concludes with these words: "I shall think myself happy if I have succeeded in impressing more firmly on the minds of my auditors this truth, which everybody is ready to enunciate but which few have undertaken to establish by strict demonstration, namely, that *there is but one chemistry, and that the laws which regulate the constitution of organic bodies apply with equal force to the compounds of mineral chemistry and mineralogy.*"

At this period in the history of the Society a considerable stimulus to activity seems to have been derived from the International Exhibition of 1862, and no doubt the presence of many foreign chemists in London contributed to that familiar interchange of views which is so conducive to the removal of misunderstandings in regard to theoretical questions. As if suggestive of the operation known as turning over a new leaf, the Journal was renumbered, and 1863 saw the

issue of the first volume of a new series. The talk was, however, still in the language of types. There was only a little more disputation as to the meaning of type formulæ, and as the types of Gerhardt and Williamson and Kekulé were found to be insufficient, condensed types and mixed types were employed. Playfair's peroxide type, on which he lectured to the Society in 1863, came too late to have any effect whatever, and never reappeared. The system of types was doomed.

Much of the discussion of the time remained barren so long as there was no agreement as to atomic weights. Notwithstanding that Kekulé and Couper, in 1858, had already shown the tetradic character of the atom of carbon, and had used formulæ in which the atoms are linked together in the same way as in modern constitutional formulæ, it was not until 1865 that a definite exposition of the doctrine of valency or atomicity in its application to the determination of the structure of molecules appeared in the *Journal* (Crum Brown, "On the Theory of Isomeric Compounds," [ii], 3, 230).

In the next volume (1866), the paper by Frankland, entitled, "Contributions to the Notation of Organic and Inorganic Compounds," shows that the time had arrived for the general adoption of the new doctrines. In the course of this paper, the author states that he has used the new notation throughout his course of lectures at the Royal College of Chemistry in the preceding autumn, although something of the same kind had been used by Frankland and Duppa two years previously.

There can be no doubt that this paper produced a great impression, at any rate in England, and the new notation was very freely discussed at the meetings of the Society and elsewhere. But, as showing how slowly the notions involved in type formulæ were modified, a paper by Griess on his diazo-compounds in the next volume of the *Journal* (1867) has a footnote in which he refers to the alternative representation of amino-compounds like phenylamine to the ammonia type and to the same type as the nitro-compounds from which they are derived. Further on in the same volume is the well-known paper by Dr. Perkin on the basicity of tartaric acid, which ends with a long array of formulæ written in conformity with the water type.

The recognition of valency and atomic linking as the basis of a system of constitutional formulæ could not, however, have been accomplished without the co-operation of many contributory investigations and conventions.

A scheme of atomic weights founded on some generally applicable principle was, before all things, necessary, and up to the time referred to no principle had been generally accepted. Cannizzaro, in 1858, had drawn attention to the application of the law of Dulong and Petit, and the law of Avogadro had been utilised, by Gerhardt especially, as the

basis of his system of formulæ. There is, however, no record in our Journal of these important proposals, and the Fellows of the Chemical Society were indebted at this period for the clarification of their ideas more to the writings and oral expositions of their then Junior Secretary, Odling, than to any other source of enlightenment.

The next great step in advance, the formulation of the theory of asymmetric carbon and the foundation of stereochemistry is represented in our Journal by two abstracts, to be found in the volume for 1875, the one entitled "Structural Formulæ," by J. H. van't Hoff, the other, "Relations between the Formulæ of Organic Bodies and the Rotatory Power of their Solutions," by J. A. Le Bel. I need not enter into the course of events which ultimately led to the complete triumph of the theory, but I recall with satisfaction the award of the Longstaff Medal last year to our colleague, Professor Pope, for a series of researches, in which he has successfully applied the fundamental ideas of stereochemistry to elements other than carbon, and has thus completed the justification of the hypothesis which we owe to the genius of Le Bel and van't Hoff.

I referred at the outset to the labours of those who, sixty years ago, were occupied in rectifying equivalents. In those days, the values assigned to many of the elements were grossly inaccurate. The work, however, still goes on, although in this our day the refinements of manipulation and the resources of our wider knowledge have reduced the errors to small dimensions. Save with regard to some of the rarer metals, it would appear that the practical limits have already been reached, if we may judge by the fact that the International Committee on Atomic Weights has during the past year found it necessary to suggest only two small corrections in the table of numbers.

The reduction of a mere list of equivalents to a harmonious system of atomic weights was not accomplished without a protracted struggle, the details of which are sufficiently well known to render unnecessary any attempt to repeat the history of it here. It can never fail to be a subject of regret, however, that the paper by J. A. R. Newlands, on "The Numerical Relations between the Atomic Weights of the Elements," read to the Society on March 1, 1866, was not printed in the Journal. In that paper Newlands clearly expressed for the first time the principle of periodicity which has since been developed and established by others.

Another event of the highest interest which immediately led to discoveries of great importance was the introduction of the spectroscope as an instrument of research. Animated by the success which had already in 1861 attended its use, every chemist of that time was more or less occupied in scrutinising all kinds of mineral matters, often with the

aid of a home-made instrument. No paper nor any formal discourse directed to an exposition of the subject, however, appeared in the Journal until the publication in that year of a translation of the Memoir by Kirchhoff and Bunsen. One of the earliest fruits of the new method was the discovery of thallium, which, observed in 1861, exhibited in the metallic state in 1862, was described for the first time in our Journal in 1864.

The settlement of molecular weights on a common foundation was another matter in which many difficulties were at first encountered. Even for those with the most definite leaning towards the doctrines of Avogadro, "anomalous" vapour densities provided a serious stumbling-block for a few years before and after 1860. It is to be regretted that no trace is to be found in the Journal of any paper or discourse relating to the general question, the difficulties of which everyone at that time recognised. A discourse was delivered by Deville in May, 1862, on Vapour Densities, but it is unreported in the Journal of the Society, and the brief notice in the *Chemical News* affords no clear idea of its scope. The same remark applies to Professor Dewar's lecture on Dissociation, given in 1874, of which no trace remains.

So large an amount of investigation carried on during recent years has been devoted to the study of the conditions which govern the rate and extent of chemical changes, that it is a source of gratification to recall the fact that one of our early volumes contains a discourse which will always rank as a classic in chemical literature, I mean Mr. Harcourt's account of his researches on the "Course of Chemical Change" (Journ. Chem. Soc., 1867, N.S. 5, 460). But even in this case it will be noticed that the first account of the work was communicated to the Royal Society, and appears in the *Philosophical Transactions* for 1866.

In 1871, at the instigation of Williamson, a very important change was introduced into the Journal by the publication of abstracts of papers appearing in foreign and other journals. This was not merely a revival of the practice, abandoned many years before, of printing abstracts of a few papers, culled rather at random from other periodicals, but a systematic attempt to present the whole of the results of world-wide research in the field of chemistry.

The Journal up to this time had been a sort of magazine containing the few original communications made directly to the Society, together with reprints from all kinds of sources. The *Philosophical Transactions* and the *Proceedings of the Royal Society* especially furnished important contributions, both as to quality and quantity. This was inevitable, so long as leaders like Hofmann, Frankland, Brodie, and others preferred to commit the results of their researches to the pages of journals of more assured position and long-established fame.

But it may also be accounted for partly by the paucity of systematic chemical research in the United Kingdom.

Frankland, in his Presidential Address in 1872, drew attention forcibly to this lack of progress. The decline in the number of papers offered to the Society having reached such a point that in the previous year only twenty-two papers had been presented seemed to justify the remonstrances of the President.

Whether Frankland was right in attributing this lethargic condition of the English chemical world wholly to the attitude of the Universities and the conditions under which degrees were granted, cannot now be discussed, but the severe remarks of another President, Dr. Perkin, in 1884, show that he was not alone in this opinion.

The question as to whether the Chemical Society provided the best medium of publication for the results of chemical research did not escape notice, and the remarks of Professor Odling, in the Presidential Address of 1875, seem to show that up to that time, at any rate, it seemed to be an accepted proposition that the Chemical Society could not expect to receive papers of the highest class representing the results of extended and laborious investigations by the most eminent workers, but must be content with discharging the useful, if somewhat humbler, function of publishing papers of more limited interest or more special character. It is otherwise now. For five and twenty years our Society has received direct communications from the most prominent and active workers, and with few exceptions the most important chemical memoirs have appeared in the Transactions, so that the Journal of the Chemical Society may now claim to be regarded as the organ of British chemistry.

Even at the present time, however, the number of papers, although large (163 from March, 1903, to March, 1904), is to the number of Fellows (2,734 in March, 1904) in about the same proportion as it has been for the last five and twenty years, namely, 1 to nearly 17.

During the sixty-two years of the life of the Society we have seen the discovery of new elements and the introduction of many new methods of experiment. Atomic and molecular weights have been distinguished, defined, and reduced to a common scale, the numerical relations among the atomic weights have been brought into a system in which the correlation of atomic mass and properties of the elements is clearly displayed. We have learnt that atoms exhibit definite and limited capacities of combination, and that certain phenomena are best explained by the assumption that atoms group themselves in definite geometrical order in space. The relation of physical properties to the constitution of compounds is now fully recognised, and to some extent traced out, while some steps have been taken toward clearer conceptions of the mechanism of chemical change. As one of the conse-

quences of the liquefaction of air and the other so-called "permanent" gases, the influence of low temperatures on the physical properties of many substances, and on the rate of chemical action, is much better understood.

What is to be the next step in advance? The subject which has occupied attention more than any other during the last two years is, of course, the phenomena presented by radioactive substances. For an account of the extraordinary properties of the substance known as radium, I cannot do better than refer to the thesis of Madame Curie, published in October and November last (*Ann. Chim. Phys.*, 1903, [vii], 30, 99—203, 289—326), which will always have great historical interest. But with regard to the hypotheses suggested by some physicists in connection with this subject, the only safe course is to reserve judgment until *the facts* have become better known. Chemists can hardly look without emotion on a scheme of the universe in which the atoms which have so long been the foundation of systematic chemistry are represented as undergoing spontaneous disintegration, although that process is supposed to be compensated by a reintegration which may result in a new order of things.

It is not possible in a breath to summarise the present state of knowledge and so to indicate the probable direction of future advance. I hope this will be done more completely and effectively by means to which I shall refer presently.

But it is interesting to compare the conditions under which scientific work is done nowadays with those which prevailed at the inauguration of this Society and for at least a quarter of a century later.

In 1841, there were practically no laboratories for instruction in this country. The teaching of chemistry was done wholly by lecture. In the University of Cambridge, the Professor of Chemistry was a country clergyman who usually visited the University once a year for a few weeks to deliver his course. The University of Oxford had a Professor of Chemistry who was also Professor of Botany. Graham was at University College, London, working actively but alone. There was neither Government Grant in those days nor Research Fund to give assistance.

At the present time, we may say even proudly that the chemical work done in this country is equal in quality and not greatly inferior in quantity to that of any other country, and that the number of universities, colleges, polytechnics, and schools is steadily increasing in which, not only is research carried on, but participation in this work is one of the avenues to degrees, scholarships, and other rewards which are open to the aspiring student. The endowment of research is always a difficult question, but the assistance afforded by our own Research Fund has undoubtedly been a means of facilitating systematic investigation by the chemists of this country. It is an object which

may fairly be commended to the notice of those who combine the possession of this world's goods with an interest in physical science. The fund is still small, and the amount distributed is annually less than the demand made upon it, chiefly for the cost of material.

In whatever direction we look, it is evident that each worker necessarily becomes more and more of a specialist with less time and power to follow the course of progress along lines other than those in which he is particularly occupied. This isolation of workers is, however, not good for anyone, and the question how each can most readily obtain information as to what is taking place in other divisions of his science is very important. In the early days of the Society some assistance was afforded by the lectures which were given rather frequently on subjects of general interest, and it was evidently considered that one of the functions of the Society was to provide this kind of instruction for its members. Special lectures have been much less frequent of late years and the only sources of general information, and that from the nature of the case, belonging chiefly to a bygone time, have been the Memorial Lectures in honour of eminent foreign Fellows deceased. I do not forget the addresses given by successive Presidents on the occasion of the Anniversary Meeting, but for a variety of reasons these have so often been directed towards other matters that it is evident the Presidential Address cannot be depended on for a review of progress or a summary of the existing state of chemical science. It is true that the Abstracts published monthly may be regarded as furnishing a tolerably complete *résumé* of chemical literature, but as each one usually deals with a detached portion of a research which is still in progress, the specialist cannot without great labour gather what he requires from any division of the subject not immediately his own. I venture therefore to make a suggestion.

It has been a growing custom with the British Association, for example, to publish reports on the present state of our knowledge in regard to selected subjects prepared by scientific men specially conversant with them. And I am encouraged by the expressions of approval in reference to such custom contained in the Address of my predecessor last year to suggest that the preparation of such reports is a matter to which the Chemical Society might advantageously give attention. Our abstracts are classified under seven heads, namely, organic, general and physical, inorganic, mineralogical, physiological, agricultural, and analytical chemistry. A report of progress during the year in each of these divisions of our science would, I believe, be very acceptable to the busy chemist, and would serve in an important degree to guide the historian of science. I propose to lay a scheme before the Council, and I hope it may be found practicable to carry this proposal into effect.

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## FARADAY LECTURE.

(Delivered before the Fellows of the Chemical Society in the Theatre of the Royal Institution on Tuesday, April 19th, 1904.)

*Elements and Compounds.*

By WILHELM OSTWALD.

I have the honour of speaking to an audience of many men whom I have long venerated as my intellectual, although not my personal, teachers, and whom I admire as leaders in our common work for science. But however admirable the *present*, I am still more impressed by the thought of the *past* associated with this place. When, not long ago, I was engaged in electrochemical investigations and almost daily sought for information and enlightenment in Faraday's Researches, I did not dare to think in my boldest dreams that one day I should find myself standing on the very spot in which he was wont to give the first accounts of the innumerable results of his indefatigable labours, his indomitable zeal, and his inexorable love of truth.

All that the pupil can do in such a case is to imbue himself as completely as he can with the ideas of the master and to try to perform his modest work in the master's spirit. But here arises a new difficulty: what subject ought I to choose? When I look into my own humble efforts, I find everywhere traces of Faraday. So far as relates to electrochemistry, the thing is plain; I think there is no word that I have oftener spoken or written than the word "ion," that word which was uttered for the first time in its modern sense in this very spot. But in other fields in which I have also worked, I feel the influence of his skilful hands and his keen vision. Catalysis, which I have studied during the past ten years, likewise came under his hands; and in the parts of the subject he worked at, the charm of secrecy and inexplicableness has been exchanged for the better qualities of a problem capable of resolution by earnest workers. And in one subject which has engrossed a very great part of my scientific activity, in the question of energy, I find the venerated master again a leader. He was indeed the first scientific man to direct all his investigations in view of the idea of the conservation and the mutual transformation of the various forces, as he called them, or the various kinds of energy, as we call them now.

This is a side of Faraday's mind, to which perhaps not so much attention has been paid as it deserves. Although doubtless the greatest advance—the discovery of the quantitative proportionality

between the energy which disappears and that which originates—was due to Mayer and Joule at a later date, yet the practical perception of this relation was working in Faraday's mind long before. There is indeed a great difference between the intellectual development of a scientific truth to a degree sufficient for the discoverer's *own* work, and to the degree required for its successful transfer to the minds of *other* workers. Faraday contented himself in this case, as well as in others (for example, in his conception of lines of force), with the first step. But that he had reached this step and stood firmly on it, that he used this conception constantly and regularly in his work, is evident from his constant reference to it from the first year of his scientific work onwards. From a closer study of his lectures and papers we learn that in every case he put the question: how can I change a given force into another? This continued to the very end of his work; for the last experiments he made related to the direct conversion of gravity into electricity, and although he did not succeed in his attempt, he was nevertheless convinced of the possibility of the conversion.

Guided by these considerations, I directed my attention to the very earliest problems treated by the master. Even before Faraday held the Chair of Chemistry here in the Royal Institution, as a youth of twenty-five years of age he practised the art of a lecturer in a small club, the City Philosophical Society, and the first course which he delivered there was on chemistry. In the sixteenth lecture, after a description of the metals, he concluded with the following general remarks:

“To decompose the metals, then, to reform them, to change them from one to another, and to realise the once absurd notion of transmutation, are the problems now given to the chemist for solution. Let none start at the difficult task and think the means far beyond him; everything may be gained by energy and perseverance.” And after a description of how in the course of history the means necessary for the isolation of the metals from their combinations have grown ever more and more efficacious, he mentioned the recent great discoveries of his master Davy as follows:

“Lastly, glance but at the new, the extraordinary powers which the chemist of our own nation put in action so successfully for the reduction of the alkalies and the earths, and you will no longer doubt that powers still more progressive and advanced may exist and put at some favourable moment the bases of the metals in our hands.”

When I try to follow this hint and take for the object of our consideration the question of the nature of the elements and of their compounds, I am aware that I am not the first who has done so in this place. If I am not mistaken, the very first chemist who had the honour of addressing you as a Faraday lecturer, Jean-Bap-

tiste Dumas, lectured 35 years ago on the same subject. Nevertheless, I do not shrink from the repetition. Every generation of chemists must form its own views regarding this fundamental problem of our science. The progress of science shows itself in the way in which this is done. Faraday was at this time fully influenced by Humphry Davy's brilliant discoveries, and sought for the solution of the problem in Davy's way. For Dumas, the most important achievement of the science of his day was the systematising of organic chemistry, condensed into the concept of *homologous series*. He therefore regarded the elements as comparable with the hydrocarbon radicles, and tried to arrange them in similar series with constant differences in the numerical values of their atomic weights. It is well known that these ideas finally developed into the great generalisation we owe to Newlands, Lothar Meyer, and Mendeléeff. Although the problem of the decomposition of the elements was not solved in this way, these ideas proved to be most efficient factors in the general development of science.

From what store of ideas will a modern chemist derive the new materials for a new answer to the old question? A physicist will have a ready answer: he will construct the elements in a *mechanical* way, or, if he is of the most modern type, he will use *electricity* as timber. The chemist will look on these structures with due respect indeed, but with some reserve. Long experience has convinced chemists (or at least some of them) that every hypothesis taken from another science ultimately proves insufficient. They are adapted to express certain sides of his, the chemist's, facts, but on other not less important sides they fail, and the end is inadequacy. Learning by this experience, he makes a rule to use only chemical material for this work, and according to this rule I propose to proceed.

Hence, like Dumas, I put the question: what are the most important achievements of the chemistry of our day? I do not hesitate to answer: *chemical dynamics* or the theory of the progress of chemical reactions and the theory of chemical equilibrium. What answer can chemical dynamics give to the old question about the nature of the chemical elements?

The answer to this question sounds most remarkable; and to impress you with the importance I ascribe to this investigation, I will mention the result at once: *It is possible, to deduce from the principles of chemical dynamics all the stoichiometrical laws; the law of constant proportions, the law of multiple proportions and the law of combining weights.* You all know that up to the present time it has only been possible to deduce these laws by help of the atomic hypothesis. Chemical dynamics has, therefore, made the atomic hypothesis

unnecessary for this purpose and has put the theory of the stoichiometrical laws on more secure ground than that furnished by a mere hypothesis.

I am quite aware that in making this assertion I am stepping on somewhat volcanic ground. I may be permitted to guess that among this audience there are only very few who would not at once answer, that they are quite satisfied with the atoms as they are, and that they do not in the least want to change them for any other conception. Moreover, I know that this very country is the birthplace of the atomic hypothesis in its modern form, and that only a short time ago the celebration of the centenary of the atomic hypothesis has reminded you of the enormous advance which science has made in this field during the last hundred years. Therefore I have to make a great claim on your unbiassed scientific receptivity. But still I do not hesitate one moment to lay the results of my work before you. For I feel quite sure that I shall find this receptivity unrestricted; and, moreover, I shall reap another advantage. For I also feel assured that you will offer me the severest criticism which I shall be able to find anywhere. If my ideas should prove worthless, they will be put on the shelf here more quickly than anywhere else, before they can do harm. If, on the contrary, they should contain anything sound, they will be freed here in the most efficacious way from their inexact and inconsistent components, so as to take the shape fittest for lasting use in science. And now let us go into the matter.

The first concept we start from is *equilibrium*. In its original meaning, this word expresses the state of a balance when two loads are of the *same weight*. Later, the conception was transferred to forces of all kinds, and designates the state when the forces neutralise one another in such a way that *no motion* occurs. As the result of the so-called 'chemical forces does not show itself as a motion, the use of the word has to be extended still further to mean that *no variation* occurs in the properties of the system. In its most general sense, *equilibrium denotes a state independent of time*.

For the existence of such a state it is above all necessary that temperature and pressure shall remain constant; in consequence of this, volume and entropy remain constant too. Now it is a most general experimental law, that the possibility of such a state, independent of time, is dependent on the *homogeneity* of the system. In non-homogeneous bodies, as, for instance, in a solution of different concentrations in different places, or in a gaseous mixture of different composition in different places, equilibrium cannot exist, and the system will change spontaneously into a homogeneous state. We can therefore limit our consideration to this state, and we shall consider

only bodies or systems of bodies in equilibrium, and, consequently, homogeneous.

Perhaps the possibility of the existence of water in contact with water-vapour might be considered contradictory to this statement, because we have here two different states and no homogeneity. Here we meet with the new concept created by Willard Gibbs, namely, that of a *phase*.

Systems of this kind are formed of homogeneous bodies indeed, but of more than one. The water in our system is homogeneous in itself, and the vapour too, and equilibrium cannot exist until both are homogeneous. But there is a possibility that a finite number of different homogeneous bodies can exist together without disturbing one another. In such a system we must have the same temperature and the same pressure everywhere, but the specific volume and the specific entropy may change from one body to the other.

We call a *phase* every part of the system where these specific properties exhibit the same value. It is not necessary that a phase should be connected to one body only ; it may be distributed over any number of parts. In this way the millions of globules of butter in milk form only *one* phase, and the watery solution of casein and milk-sugar forms a second phase : milk is a two-phase system.

*Every system consisting of only one phase has two degrees of freedom.* This law involves only the assumption that the sole forms of energy involved in the system are heat and volume-energy ; we exclude from consideration any effects due to gravitation, electricity, surface-tension, &c. This law is connected with the famous phase rule of Willard Gibbs, but is not identical with it, for it contains no mention at all of the so-called components of the system. Indeed, the law is valid in the same way for any pure chemical element, for example, oxygen, or for any mixture, for example, a glass of whisky and water. If you allow to the latter only one phase, it is impossible to change it in more than two ways, namely, in pressure and temperature.

The existence of such a body in the shape of only one phase is generally limited. If the pressure be lowered at constant temperature, a liquid or a solid will change at last into a gas. Lowering of temperature will change a gas into a liquid and a liquid into a solid. For every one-phase system it is possible to determine a "sphere of existence." This sphere is not necessarily limited on all sides ; for gases we do not expect a limit on the side of low pressures and high temperatures, nor for solids on the side of high pressures and low temperatures. But on certain sides every phase has its limits, and most of these limits are experimentally accessible.

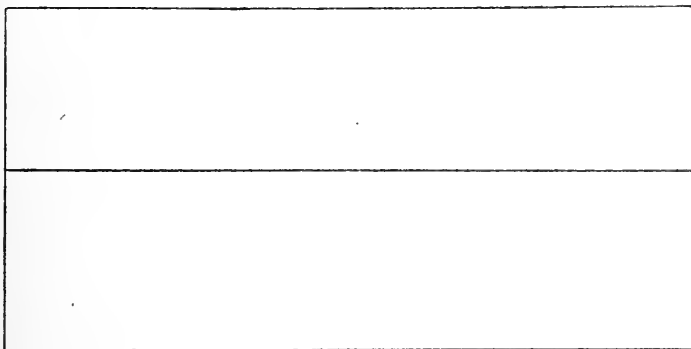
What will happen if we exceed the limit of existence of a phase?

The answer is most simple: *a new phase will be formed*. The spheres of existence of the different phases therefore limit one another, and the boundary-lines represent the interdependent values of temperature and pressure for the possibility of the co-existence of both phases.

By granting the co-existence of two phases we lose therefore one degree of freedom. At the same time a new variation has arisen from the ratio between the masses of the two phases. For we must not suppose that this ratio is without influence on the state; indeed we find here two radically different cases.

The most general case is, that during the transformation of one phase into another the properties of both are continually changing, and the state of every phase is therefore dependent on the ratio of the two masses. By evaporating sea-water at constant temperature the

FIG. 1.



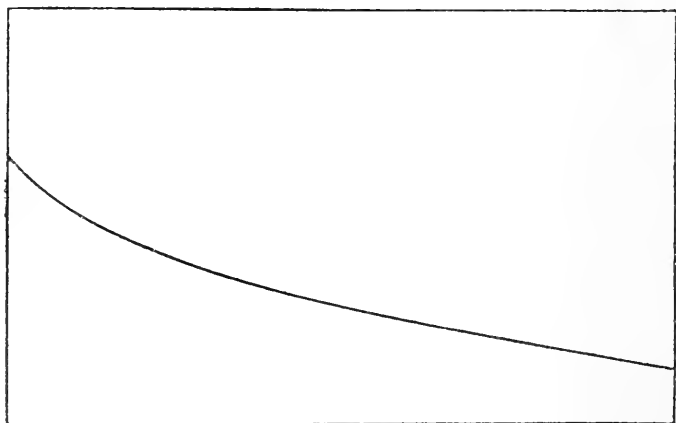
density of the residue grows continually higher, while the pressure, and therefore the density, of the vapour goes on decreasing. If, however, we evaporate distilled water, we do not find any change in the properties of the residue and of the vapour during the whole transmutation.

Bodies of the first description we will call *solutions*, and of the second, *hylotropic bodies*. You will be inclined to call the latter substances or chemical individuals, and indeed both concepts are most nearly related. However, the concept of a hylotropic body is somewhat broader than that of a substance. But the possibility of being changed from one phase into another without variation of the properties of the residue and of the new phase is indeed the most characteristic property of a substance or chemical individual, and all our methods of testing the purity of a substance or of preparing a pure one can be reduced to this one property; any one may readily convince him-

self of this by investigating any such method in the light of this description.

If we represent these cases by means of rectangular co-ordinates, taking as abscissæ the part of the first phase converted into the second, and as ordinates pressure or temperature, we get Fig. 1 (p. 6) for hylotropic bodies; they are represented by a horizontal straight line. With a solution we get a continuous line too, but not horizontal and generally not straight. If the ordinates are pressures at constant temperature, and the change is from liquid into vapour, the line will slope downwards as Fig. 2 shows. At other temperatures the lines will be of similar shape, only lying higher at higher temperatures and *vice versa*. With other changes we obtain similar lines, sloping upwards or downwards as the case may be. For simplicity's sake we

FIG. 2.



will consider in the future only vaporisation; this case gives the greatest possible variety, and we are sure not to omit anything by such a limitation.

What is the general process of change in a solution while it is being vaporised? The answer is quite distinct: *the residue is always less volatile* than the original solution, and *the distillate more volatile*. If there were an example of a solution behaving in the contrary way, then the process of vaporisation at constant temperature would be an explosive one. For the vapour begins to form at a given pressure; if by this the vapour-pressure of the residue were lowered, the vaporisation would continue of itself at a continually accelerated rate until all the liquid would be vaporised at once. It would be, in other words, a *labile* equilibrium. These equilibria are, however, only mathematical fictions, and have no experimental existence. If, on

the contrary, the residue has a lower vapour-pressure, then the process is self-limiting, and shows the characteristics of a *stable* equilibrium. With hylotropic bodies we have an *indifferent* equilibrium, because the state is independent of the progress of the transmutation.

This being granted, we can ask: if we continue the separation of a solution into a less and a more volatile part by repeated distillation, what will finally become of it? Generally considered, two cases may happen. First the residue may become less and less, and the distillate more and more volatile, and there is no end to the progress. This case we may exclude from experimental evidence of a most general character, for we may take it as a general law that it is impossible to enhance any property beyond all limits, even by the unlimited application of our methods. We must conclude, therefore, that we shall ultimately meet with a *limit of volatility on both sides*, that finally we shall have separated our solution into a least and a most volatile part, and that both parts will not change further by repeated distillation. This is a most interesting result, for it means that *every solution can be resolved into components, which are hylotropic bodies*. For simplicity's sake we have considered only the case that two hylotropic components are generated by the process of separation; generally more than two may be formed, but in every case only a limited number of such components is possible. We may formulate therefore as a general law:

*It is possible in every case, to separate solutions into a finite number of hylotropic bodies.*

From the components, we can compose the solution again with its former properties. This is also a general experimental law; if exceptions seem to exist, it is only because the case is not one of true equilibrium. Still we may limit our consideration to those cases where the law holds good. Then we have a relation between the properties of any solution, and the nature and relative quantity of its hylotropic components, which admits of only one interpretation. Every solution of distinct properties has also a distinct composition and *vice versa*.

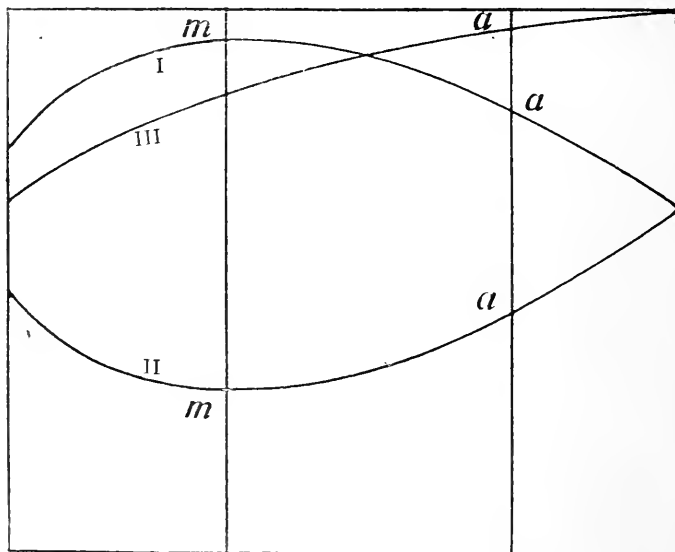
If we consider for simplicity's sake solutions of only *two* components, we may represent any property as depending upon the composition in a rectangular co-ordinate system, the abscissæ giving the composition and the ordinates the value of the property considered. In this way, we get a continuous line of a shape dependent on the particular case chosen.

If we consider the boiling points of all solutions formed by two hylotropic components, the most simple forms of curves (indeed the only experimental ones known) are given by the types I, II, and III, Fig. 3. For any solution, for example, the solution with the abscissa *a*, we can foretell its variation on distillation by the slope of the curve. For as

the residue must be less volatile, the residue will change to the ascending side of the curve. This is for I and III to the right, for II to the left side of the diagram. The change of the *distillate* is the opposite.

If we try to apply this criterion to the points *m* of the curve II and III, where there is a maximum and a minimum of the boiling point, we arrive at no decisive answer, for if the boiling point is already the highest possible it cannot rise, and if it is the lowest possible, it cannot fall. We are forced therefore to conclude that the boiling

FIG. 3.



point cannot change at all, that is, that this special solution must behave as a hylotropic body.

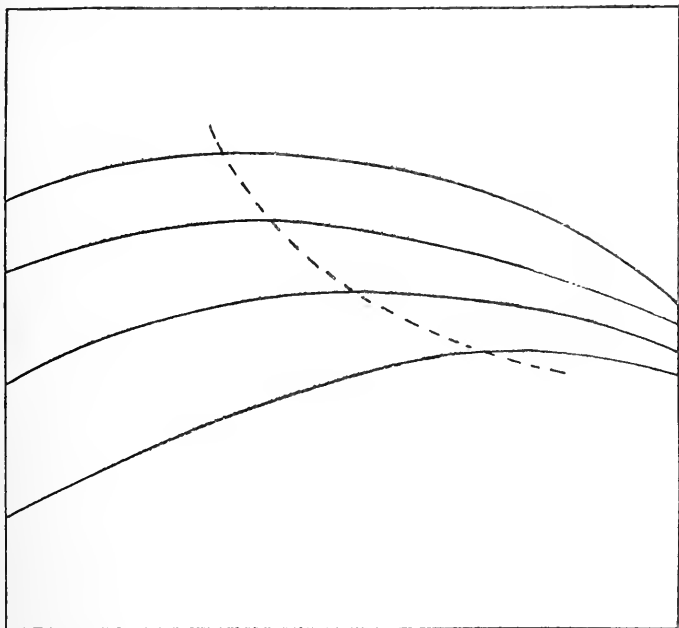
This is a well-known theorem of Gibbs and Konovaloff, to wit, that a maximum or a minimum, generally spoken of as a *distinguishing point* in the boiling-curve, is necessarily connected with the property of distilling without change in the composition of the solution. A similar law holds good for the transitions from liquid to solid and from solid to gas.

Now this looks like a contradiction; while a few minutes ago we placed solutions in a class exclusive of hylotropic bodies, we have here solutions, that is, mixtures, which behave like hylotropic substances. But the contradiction vanishes if we consider a series of boiling-point curves corresponding with various pressures. We then find that the composition at the distinguishing point does not remain constant under different pressures, but shifts to one side, with alteration of pressure. This fundamental fact was discovered and experimentally

developed in an admirable way by Sir Henry Roscoe, and has since proved itself a most important criterion in recognising a chemical individual.

By drawing curves corresponding with various pressures, we get therefore generally the diagram shown in Fig. 4, the loci of the distinguishing points forming one curve. Between the infinite possibilities of the shape of this curve we have a distinguishing case again, the case that the curve is a *vertical straight line*. This means that the composition

FIG. 4.



is independent of the pressure. When this is the case, we call this *hylotropic body a substance or a chemical individual*.

Therefore we conclude that a connection exists between solutions and chemical compounds or substances ; the latter being a distinguishing case of the former. On the other hand, we get an exact definition : *a substance or a chemical individual is a body, which can form hylotropic phases within a finite range of temperature and pressure*.

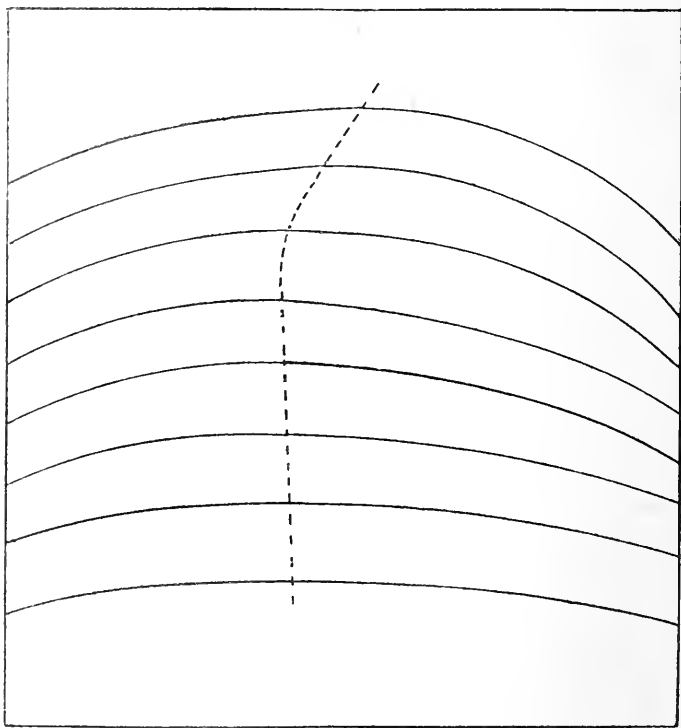
Such substances can often be produced from other substances in the same way as a solution is, namely, by putting them together. If that can be done, we may infer from our definition that there exists a definite ratio between the components, independent of temperature and pressure between certain limits.

Now, *this is essentially the law of definite proportions*, the first of the stoichiometrical laws. We have deduced, therefore, the law of constant proportions from the concept of the chemical individual.

As you have seen, this deduction is extremely simple; the constancy of composition is a natural consequence of the mode of preparation and purification of chemical substances.

If we exceed the limits of temperature and pressure, where the

FIG. 5.



body behaves as a hylotropic one, it assumes the properties of a solution, that is, its distinguishing point begins shifting in composition when the temperature is changed. Then it becomes possible to separate the body into its components, and we call this state the state of dissociation of the substance in question. In our graphic representation, the hitherto straight vertical line of distinguishing points turns sideways, Fig. 5.

Most substances behave in this way, but there are substances which have never been transformed into solutions or whose sphere of existence covers all accessible states of temperature and pressure. Such

substances we call elements. In other words, *elements are substances which never form other than hylotropic phases.*

From this we may conclude that every body is finally transformable into elements, and into only *one definite set of elements.* For the most general case is a solution. Every solution can be separated into a finite number of hylotropic components, and these again can generally be transferred into a state when they behave like solutions and can be separated further. Finally, the components remain hylotropic through the whole range of temperature and pressure, that is, they are elements.

From the fact that the relation between a compound substance and its elements admits of only one qualitative and quantitative interpretation, we derive the conclusion that the resolution of any substance into its elements must always lead to the same elements in the same proportion. Here we find the source of the law of the *conservation of the elements.* This law is not generally expressed as a special stoichiometrical law, because we tacitly infer it from the atomic hypothesis. But it is truly an empirical law, and we see that it is not only a consequence of the atomic hypothesis, but also a consequence of the experimental definition of an element and of our methods of obtaining elements.

Here I should like to pause for a moment for the purpose of quoting a couple of historical facts. Up to the present moment, the question whether it is possible to deduce the stoichiometrical laws without the help of the atomic hypothesis has only been raised by other investigators in order to deny the possibility. So far as I am aware, there exists only one man who has worked upon the question with the earnest hope of obtaining an affirmative answer. Very few know his name. The man is Franz Wald ; he is chief chemist at the iron works in Kladno, Bohemia. His papers on the subject are to be found in the *Zeitschrift für physikalische Chemie* and in the *Annalen der Naturphilosophie.*

In the foregoing considerations, Franz Wald has played a great part. To him I owe first the idea that the definition of substances and elements is in a certain sense arbitrary, although very helpful and convenient. This definition is a condensed expression of our methods of separating and purifying these bodies. While, generally speaking, every solution has the same claim to be investigated as these bodies, the latter soon distinguish themselves as standards to which all other cases may be referred. To Franz Wald I owe further the idea that the conception of a *phase* is a far more general one than that of a substance, and that the deduction of the idea of a substance, and, further, the deduction of the laws governing the nature of substances, must start from the conception of the phase. I do not know whether

Wald will agree with the way I have made use of his ideas, but I feel it imperatively necessary to express my deep respect for, and my thankful obligation to, this solitary philosopher, who has prosecuted his work during a long series of years almost wholly without encouragement or sympathy from others.

Now there are still two stoichiometrical laws to be deduced, namely, the law of multiple proportions and the law of combining weights. I prefer to invert the order, and first to deduce the second law. It expresses the fact that it is possible to ascribe to each element a certain relative weight in such a way that every combination between the elements can be expressed by these weights or their multiples.

We suppose three elements, A, B, and C, given, which may form binary combinations, AB, BC, and AC, and besides these a ternary combination, ABC; there shall be but one combination of every kind. Now we begin by forming the combination AB; for this purpose, we must take a certain invariable ratio between the weights of A and B, according to the already proved law of constant proportions. Now we combine AB with C and get the ternary compound, ABC. There will be a certain ratio, too, between AB and C, and we can, if we put A as unity, assign to B and C certain numbers describing their combining weights relatively to A.

Now we begin to combine A with C forming AC, and then we form the ternary combination, ACB from AC and B. According to our law of a relation between elements and compounds, which can be interpreted only in one way, ACB cannot be different from ABC, and, in particular, it must show the same ratio between the relative weights of its elements. Therefore, the ratio of the weights of A and C in forming the combination AC cannot be other than that expressed by the relative combining weights already found in the first way. In other words, it is possible to compute the composition of the hitherto unknown combination AC, from analyses of the combinations AB and ABC. In the same way, we can compute the composition of the unknown combination BC, by the help of the numbers obtained by the analyses of two other combinations of the same elements. To resume: the combining weights relatively to A regulate all other possible compounds between the elements concerned. But this is nothing else than the general stoichiometrical law of combining weights for we can extend our considerations without difficulty to any number of elements.

Lastly, it is easy to deduce the law of multiple proportions from the law of combining weights. If no compounds can be formed except according to their combining weights, then, if there are two different compounds between A and B, we can form the one containing more of B either directly from A and B, or indirectly, combining first A and B

to form the lower compound and then combining this with more of B. In applying the law of combining weights, we conceive that the weight of B in the higher compound must be twice its weight in the lower. The same consideration may be repeated, and finally we get the result, that instead of double the combining weight, *any multiple* of it may occur in combinations, but no other ratio.

If we cast a backward glance on the mental operations we have performed in the last two deductions, we recognise the method, the application of which has made the two laws of energetics so fruitful. In the same manner as the difference between the whole and the available energy is independent of the nature of the path between the same limiting points, the product of the chemical action between a number of given elements is independent of the way in which they are combined. If we compare two different ways, we get an equation between the characteristics of the two ways, and this is equivalent to a new law. In our case, this new law is the law of combining weights.

I will put the same idea into somewhat different words. By stating the equation between any two ways, we can get any number of different equations, each representing a new way as an experimental fact. Now, in order that all these equations shall be consistent, there must be some general law regulating the characteristics of the equations. For the consistency of the several equations in the case under discussion, the existence of specific combining weights, independent of the several combinations, is the necessary condition.

This is the main point of the considerations I wish to lay before you this evening. There are some secondary questions as to isomerides or allotropic states of substances, and there are other similar questions, but it would lead us too far to consider them one by one. I have investigated them on the same basis, and I can assure you that I have nowhere found an insurmountable difficulty or an impassable contradiction. All these facts find their proper place in the frame of the same general ideas.

Let me still add some words about the *nature of the elements*, as considered from my point of view. I wish to lay great stress on the fact that here, too, I find myself on the same ground as that on which Faraday has built his general concepts during his whole scientific career. There is only one difference, due to the development of science. Faraday ever held up the idea that we know matter only by its forces, and that if we take the forces away, there will remain no inert carrier, but really nothing at all. As Faraday still clung to the atomic hypothesis, he was forced to express this idea by the conception that the atoms are only mathematical points whence the forces emerge, or where the directions of the several forces intersect; here his view coincided with that of Boscovich.

In the language of modern science I express these ideas by stating: *what we call matter is only a complex of energies which we find together in the same place.* We are still perfectly free, if we like, to suppose either that the energy fills the space homogeneously, or in a periodic or grained way; the latter assumption would be a substitute for the atomic hypothesis. The decision between these possibilities is a purely experimental question. Evidently there exist a great number of facts—and I count the chemical facts among them—which can be completely described by a homogeneous or non-periodic distribution of energy in space. Whether there exist facts which cannot be described without the periodic assumption, I dare not decide for want of knowledge; only I am bound to say that I know of none.

Taking this general point of view, in what light do we regard the question of the elements? We will find the answer, if we remember that the only difference between elements and compounds consists in the supposed impossibility of proving the so-called elements to be compounds. We are therefore led to ask for the general energetic properties underlying the concept of a chemical individual, whether element or compound.

The answer is most simple. The reason why it is possible to isolate a substance from a solution is that the available energy of the substance *is a minimum*, compared with that of all adjacent bodies. I will not develop this thesis at length, for it is a well-known theorem in energetics or thermodynamics. I will only recall the fact that a minimum of vapour-pressure is always accompanied by a minimum of available energy; and we have already seen that a minimum of vapour-pressure or a maximum of boiling-point is the characteristic of a hylotropic body or chemical individual.

This granted, we proceed to the question regarding the differences between the several substances. Expressed in the most general way, we find these differences connected with differences in their *specific energy content*. Temperature and pressure are not specific, for we can change them at will. Specific volume and specific entropy, on the contrary, are not changeable at will; every substance has its own values of these. We may take therefore these values as the characteristics of the different substances. How many of such characteristics exist I cannot tell. Only for simplicity's sake I will assume that two of them are sufficient. As I will take care not to deduce any conclusions from this number, we shall not be led into error by accepting it.

We place these two characteristics in a system of planar co-ordinates; then the several elements will be represented by single points in the plane. We lay the plane horizontally and raise from these points ordinates, representing the available energy of each element. Between the points of the elements in the plane are situated the

points of all possible solutions, filling up the whole plane. Each of these solutions will also have its available energy, and all the corresponding points in space will form a continuous surface. The form of this surface can be described in a general way. For as each *element* has its point in a *relative minimum*, the surface as a whole will have a shape like the ceiling of a cavern full of hanging stalactites, the end of each stalactite representing an element.

How can we pass from one element to another? Evidently not otherwise than by going over the higher parts of the surface, or the passes separating each stalactite from its neighbours. This can only be done by accumulating an appropriate amount of available energy in the element to be changed. Now the concentration of energy is a task we cannot accomplish *ad libitum*, for the possibility very soon ends. Think, for example, of compressing a gas into a given space. Up to some ten thousand atmospheres the work of compression will go on smoothly, but after that every metal begins to flow like a liquid and you cannot proceed further. With the concentration of electric or any other energy the task is similar and so we come to the conclusion that the concentration of energy can be pushed to only a very limited extent. The application of this result to our question about elements is simple enough: we cannot get over the pass between two stalactites because we cannot attain the necessary concentration of energy.

From the history of science we learn that these considerations contain at least some truth, for the isolation of the elements has ever been dependent upon the power of concentrating energy available at that time. The most brilliant example is the application of the voltaic pile to the isolation of the alkali metals by Humphry Davy.

Still I must confess that these last considerations are in a very embryonic state, and I should not have brought them before you if an unexpected application had not lately made itself manifest. Some years ago I explained these views to my old friend Sir William Ramsay, when he asked me how the idea of elements fitted into my conceptions of energy. Then I forgot all about it until Sir William reminded me of it, saying that his perplexing discovery of the transmutation of radium into helium might conceivably find some explanation in this way. This I am convinced of, and the considerations may be pictured in the following manner.

In the corner of our cavern where the elements with the highest combining weight are assembled, the stalactites are very short; and at last they are not really stalactites, but rather regions of different slope in the sloping ceiling. In our cavern, a drop of water furnishes generally a picture of the stability of the elements. While hanging at the end of a true stalactite, more or less work must be done

to raise the drop over the pass until it flows down another stalactite. But in this corner it will flow of its own accord, and only delay for a short time on the nearly horizontal portions in the ceiling.

Such elements will have only a *temporary existence*. Now we are sure that for the transmutation of one element into another, enormous amounts of energy would be required, for the concentrations of energy as yet available have proved themselves insufficient for this purpose. We may expect, therefore, that enormous amounts of energy will be liberated if such an unstable element changes into a stable one. This accounts for the extraordinary quantity of energy developed by radium during its existence. The fact that radium changes into helium, an element with an exceptionally long stalactite (for it is impossible to get even any combination of helium) makes us expect indeed such an unusually great development of energy as is found to occur.\*

The heat from radium is surely only the last form of the energy developed in its transformation. There are a great many intermediate forms, termed rays or radiations, which have been studied by a band of eminent workers, whose ingenuity and ability have been displayed in the most brilliant way during these investigations. Perhaps I may venture the suggestion that first, other intermediate temporary elements are formed and that the energy liberated at this transmutation appears first in the shape of *new*, still imperfectly known forms. It is most likely that such forms are originated during the decay of the enormously concentrated energy of radium; at the same time it is probable that we have not yet the means of fixing these forms and so preventing their changing into other, more common forms. We should remember that, for example, the conservation of electric energy at a pressure of some thousand volts during some months or years is by no means an easy thing, and I have great doubt if it is possible at all.

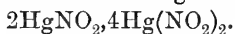
But here I must conclude, for I have ventured to intrude on a field where I have not secured my own right of entry by personal work. I see among my audience men who are possessed of an incomparably more minute and comprehensive knowledge of these new realms of science than I. I must ask you, therefore, to take these suggestions in the same spirit as that in which Faraday took his own speculations. They are questions put to nature. If she says Yes, then we may follow the same path a little further. If she says No—well, then we must try another path.

\* Compare Soddy, "The Wilde Lecture," *Mem. and Proc. Manchester Lit. and Phil. Soc.*, 1904. I am very glad to find that I am in close agreement (except in so far as there is a difference in his accepting the atomistic, while I hold by the energetic point of view) with this most zealous worker; indeed, the above statements were written and printed before I saw Mr. Soddy's lecture.

### LII.—*Mercuric Nitrite and its Decomposition by Heat.*

By PRAFULLA CHANDRA RÂY, D.Sc. (Edin.).

It has been shown (Trans., 1897, 71, 340) that when mercurous nitrite is treated with water, it undergoes the following dissociation,  $\text{Hg}_2(\text{NO}_2)_2 = \text{Hg} + \text{Hg}(\text{NO}_2)_2$ , but only to the extent of about 78 per cent., the rest going into solution along with the mercuric nitrite to form a mercurioso-mercuric nitrite having the formula



When the mercurous mercury is removed from solution by sodium chloride, a sodium mercuric nitrite is formed, from which dimercur ammonium nitrite has been obtained (Trans., 1902, 81, 644). But all attempts to isolate mercuric nitrite itself in the solid state have hitherto been unsuccessful.

Lang tried to prepare mercuric nitrite by means of the double decomposition occurring between mercuric chloride and silver nitrite, but obtained, on evaporating, a basic salt to which he assigned the improbable formula  $3\text{HgO}, \text{N}_2\text{O}_3, \text{H}_2\text{O}$  (*Kongl. Svenska Vet. Akad. Handl.*, 1860; *J. pr. Ch.*, 1862, 86, 295). A repetition of Lang's experiment, with certain modifications, has now not only yielded the normal salt,  $\text{Hg}(\text{NO}_2)_2$ , but has also shown that the cause of Lang's failure was the interesting decomposition which mercuric nitrite undergoes when gently heated.

Silver nitrite being very sparingly soluble in the cold, and heat acting prejudicially on a solution of mercuric nitrite, the following method was found, after repeated trials, to be the best for preparing mercuric nitrite.

Silver nitrite, purified by recrystallisation, and pure mercuric chloride are weighed out in molecular proportions and rubbed together in a mortar to a fine paste with water, a little more water being gradually added with continued stirring. The mass is then washed into a stoppered bottle and violently agitated. It is well known that silver nitrate does not remove the whole of the chlorine from a solution of mercuric chloride; silver nitrite behaves in a like manner, and, therefore, the solution thus prepared contains unavoidably a very little silver nitrite, but not enough to be troublesome.

The pale yellow solution of mercuric nitrite, thus obtained, cannot be evaporated on a water-bath without the salt decomposing to a considerable extent, but on concentrating the solution *in vacuo* over sulphuric acid, the salt crystallises in tufts of fine needles. The salt thus obtained is contaminated only with traces of silver nitrite. By

the analysis of two distinct preparations, its composition was found to conform with the formula  $\text{Hg}(\text{NO}_2)_2$ .

	Found.		Calculated.
Mercury .....	67.81	69.13	68.49 per cent.
Nitrogen .....	9.35	9.46	9.59 ,,

Mercuric nitrite has a light yellow colour ; it dissolves only partially even in boiling water, the larger proportion decomposing into mercuric oxide and nitrous acid. When kept exposed in the air, it slowly liquefies, and gives off nitrous fumes. When treated with a solution of caustic alkali, the solid salt yields mercuric oxide, whilst the whole of its nitrogen is obtained in solution as nitrite. This is proved by the fact that the nitrogen in the filtrate, when estimated by the Crum-Frankland method, is the same in amount as when measured by the "urea" process. Mercuric nitrite is not stable in presence of air, even when preserved in a stoppered bottle inside a desiccator ; it slowly evolves nitrous fumes, and if the stopper is loosened so as to allow the fumes to pass out and be absorbed by the sulphuric acid, the salt is transformed, in course of time, into a white powder of basic mercuric nitrate. In this respect, mercuric nitrite affords a striking contrast with mercurous nitrite, since the latter keeps well for years in a dry atmosphere. When exposed in a vacuum over sulphuric acid, before it has begun to change, the salt shows, however, no tendency to decompose if left undisturbed, but decomposition, when once begun, cannot be arrested.

If the original solution of mercuric nitrite is kept for some time in a stoppered bottle which is opened from time to time, the salt undergoes, but only to a very limited extent, much the same change as that presently described, which happens to it when heated in the solid state. Thus, a solution of sp. gr. 1.065 in the course of three weeks gave the proportion of mercuric to mercurous mercury as 13.7 : 1. If, however, the solution is preserved in a tube which has been exhausted of air and then sealed up, the salt remains absolutely undecomposed.

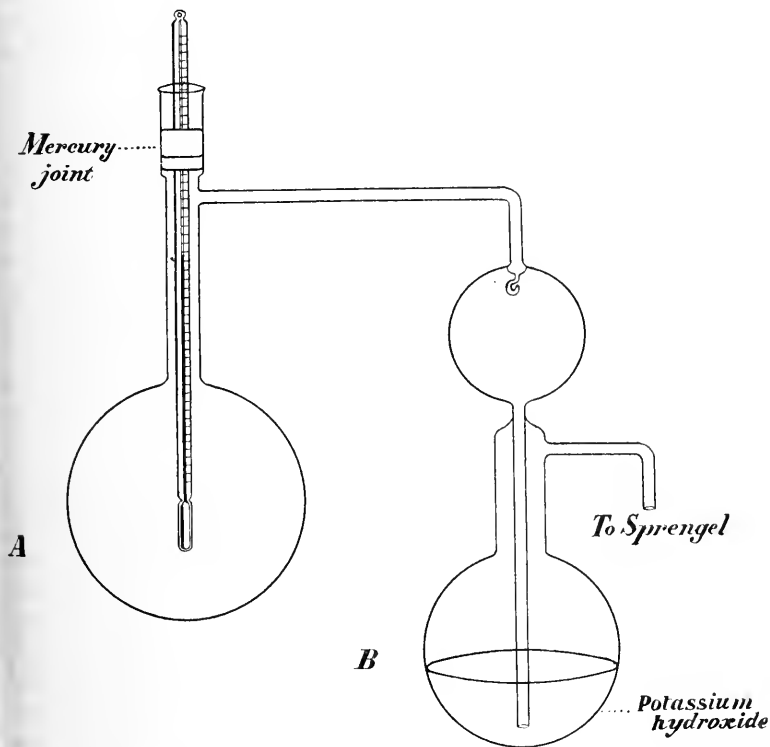
In its original solution, mercuric nitrite does not give any precipitate of oxymercuric sulphate with sodium sulphate, a fact which points to the "nitronic" constitution of the salt.

*Decomposition by Heat.*—A solution of mercuric nitrite, when evaporated on the water-bath, decomposes in two ways. The residue near the edge of the deposit consists almost wholly of crystalline, red mercuric oxide, whilst that in the middle of the deposit is a mixture of mercurous nitrate and undecomposed mercuric nitrite, with only traces of the oxide. It is probably this mixture which Lang took to be the basic nitrite he describes. For purposes of comparison, a solution of mercuric nitrate was similarly evaporated to dryness on the water-

bath ; this time the residue consisted of colourless crystals of mercuric nitrate interspersed with yellow streaks, indicating the partial formation of a basic salt. It will thus be seen that mercuric nitrite behaves in quite a different manner from the nitrate.

In order to study this decomposition more carefully, the following method and apparatus were devised.

The bulb, *A* (see fig.), contained from 5 to 10 c.c. of the solution of mercuric nitrite, whilst a dilute solution of potassium hydroxide was



placed in the bulb, *B*. The use of this alkali was necessary in order to protect the mercury in the pump from the action of the mixed gases, but it also served as a means of ascertaining whether any nitric oxide was being evolved other than that liberated by the decomposition of the nitrous anhydride produced. After the apparatus had been exhausted, the bulb, *A*, was gently heated, taking care that the temperature did not rise above  $60^{\circ}$ . Until the evaporation of the liquid was completed, very little gas was given off, in fact not more than 0.5 c.c. But the solid salt began to decompose rapidly, giving off

gas which was almost entirely absorbed by ferrous sulphate solution. The residue was found to consist of a mixture of mercurous nitrate and mercuric nitrite with only a small proportion of mercuric oxide, and no mercury whatever in the free state.

A similar result was obtained when solid mercuric nitrite was put into the apparatus and heated by keeping the bulb *A* immersed in water, the temperature of which was gradually raised to the boiling point. When the temperature had risen to 95°, the salt fused and intumescenced; then nitric oxide was for some time regularly evolved, but ultimately the gas in the bulb became reddish-brown. The gas, which was treated and collected as before, was found to be almost entirely soluble in ferrous sulphate solution, whilst the solid residue consisted mainly of mercurous nitrate. The ratio of the nitrogen as nitrate to that as nitrite was as 4.33 : 1.

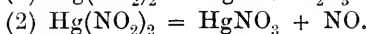
It will thus be seen that when the solid salt is heated it decomposes chiefly into mercurous nitrate and nitric oxide, thus:  $2\text{Hg}(\text{NO}_2)_2 = 2\text{HgNO}_3 + 2\text{NO}$ , only a small quantity decomposing into mercuric oxide and nitrous anhydride.

It might be supposed, firstly, that mercuric nitrite in the solid state really decomposes at first into mercurous nitrite and nitric peroxide, thus:  $2\text{Hg}(\text{NO}_2)_2 = \text{Hg}_2(\text{NO}_2)_2 + 2\text{NO}_2$ , just as auric chloride breaks up into aurous chloride and chlorine; secondly, that the mercurous nitrite thus formed decomposes into free mercury and nitric peroxide; and, lastly, that these, by their interaction, give rise to the mercurous nitrate and nitric oxide actually obtained (Trans., 1903, 83, 491).

In order to settle this point satisfactorily, the earlier experiment with mercurous nitrite (*loc. cit.*) was repeated in the new apparatus. At 100° there was no appreciable amount of gas evolved. It was only when the bulb was directly heated by the flame and the temperature exceeded 200° that the decomposition took place. In this case the resulting mercurous nitrate was deposited in thin needles, interspersed with minute globules of mercury, on the bulb and stem of the thermometer, whilst, when the reaction is carried on in a short horizontal tube, the crystals of mercurous nitrate shoot forth from the upper side of the tube. In this case, as formerly pointed out, a portion of the vapour of the mercury acting on the nitrous fumes gives rise to mercurous nitrate, the remainder being deposited in globules. Heat thus acts on mercurous and mercuric nitrites in entirely different ways, the mercurous nitrate being produced as a pseudo-sublimate in the case of the former salt, whereas it is produced in the mass of the decomposing salt in the case of the latter compound.

The present investigation shows that when a solution of mercuric nitrite, obtained by double decomposition between mercuric chloride

and silver nitrite, is concentrated *in vacuo* over sulphuric acid, it yields the normal salt, mercuric nitrite; and that when this salt is heated at 100°, it breaks up in two ways as indicated by the equations,



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### LIII.—*The Reduction of 2:6-Dinitrotoluene with Hydrogen Sulphide.*

By JULIUS BEREND COHEN and JOSEPH MARSHALL.

IN the course of an experiment in which 2:6-dinitrotoluene was reduced with hydrogen sulphide in alcoholic ammonia, a quantity of 6-nitro-2-amino-*m*-cresol was obtained together with 6-nitro-*o*-toluidine, these substances being separated in the following manner. The product, after reduction, was boiled with dilute hydrochloric acid and separated by filtration from sulphur. On adding ammonia in excess to the filtrate in order to precipitate the nitro-*o*-toluidine, a deep violet solution was obtained. The filtrate from the base was carefully neutralised, when a brown, crystalline precipitate was deposited, which was crystallised from alcohol. The new substance crystallises in dark, orange-coloured needles, which dissolve readily in dilute acids and alkalis and melt with decomposition at about 190°; it is completely precipitated by carbon dioxide from its solution in alkalis. With the mineral acids it forms well-crystallised, colourless salts; the hydrochloride crystallises in flat prisms with pointed ends, the sulphate, in fine needles, and the nitrate in clusters of acicular crystals. The compound is evidently an aminophenol and the analysis indicates a nitroamino-cresol.

0.1468 gave 22 c.c. moist nitrogen at 25° and 735 mm.  $N = 16.73$ .

$\text{C}_7\text{H}_8\text{O}_3\text{N}_2$  requires  $N = 16.56$  per cent.

In order to determine the relative positions of the amino- and hydroxyl-groups, the compound was dissolved in dilute sulphuric acid and oxidised with an excess of lead peroxide at a temperature of about 60°. The orange-coloured liquid was extracted with ether, and on removing the solvent a mass of dark red crystals remained which had the characteristic odour of quinone. On crystallisation from a mix-

ture of ether and light petroleum, the substance was deposited in the form of brilliant, ruby-red prisms which melted at 64—65°.

0.1801 gave 13.2 c.c. moist nitrogen at 17.5° and 747.5 mm.  $N = 8.54$ .

$C_7H_5O_4N$  requires  $N = 8.49$  per cent.

When sulphur dioxide is passed through the quinone suspended in water, it dissolves to a yellow solution from which ether extracts the corresponding quinol; on removing the solvent the quinol is deposited in the form of bright scarlet needles which may be crystallised from ether and light petroleum and melt at 117—118°.

The solution of the quinol in caustic soda has a deep violet colour which disappears on saturating with carbon dioxide, the quinol being regenerated. When the nitroaminocresol is dissolved in dilute hydrochloric acid and a solution of bleaching powder gradually added, a light brown precipitate is formed, which separates from a mixture of ether and light petroleum in clusters of pale yellow, spear-shaped crystals melting at 70—71°. The compound is a chloronitrotoluquinone,  $CH_3 \cdot C_6HO_2Cl \cdot NO_2$ .

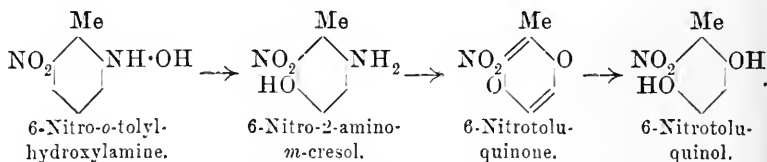
0.1352 gave 0.096 AgCl.  $Cl = 17.67$ .

$C_7H_4O_4NCl$  requires  $Cl = 17.61$  per cent.

The formation of nitroaminocresol from 2:6-dinitrotoluene is readily explained. Cohen and Dakin have shown (*Trans.*, 1902, 81, 26) that *s*-trinitrobenzene and 2:4:6-trinitrotoluene are readily reduced by hydrogen sulphide in faintly alkaline solution and yield the corresponding dinitrohydroxylamine compounds.

If the reduction of the 2:6-dinitrotoluene is not complete, 6-nitro-*o*-tolylhydroxylamine is formed and is converted by the boiling hydrochloric acid used in the extraction, into nitroaminocresol in the same way that phenylhydroxylamine yields *p*-aminophenol (Bamberger, *Ber.*, 1894, 27, 1349).

The series of changes which have been described may be represented by the following formulæ:

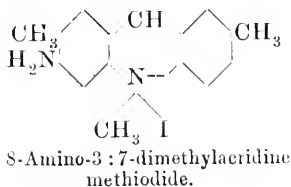
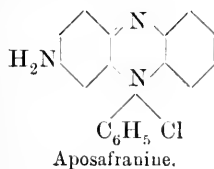


We propose to continue the investigation of the above compounds and to extend the study of the action of hydrogen sulphide to other nitro-compounds.

# LIV.—*Studies in the Acridine Series. Part I.*

By JOHN JACOB FOX and JOHN THEODORE HEWITT.

THIS paper is the first instalment of a series of communications describing the results of an examination of various acridine and azine compounds, which has been undertaken with the view of elucidating the constitution of the anhydrous bases obtained from quaternary ammonium compounds in which the quinquevalent nitrogen atom is a member of a ring attached to a benzene or naphthalene residue, this nucleus containing a substituent amino- or hydroxy-group in the meta- and para-positions relatively to the basic nitrogen atom and the remaining member of the heterocyclic ring respectively. The following substances have this configuration :

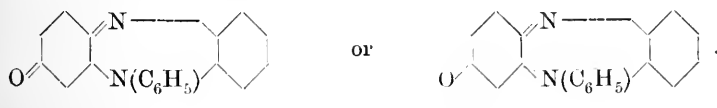


To the base obtained from the former salt the two following formulæ have been assigned,



the latter being remarkable in that a linking is supposed to occur between the substituent groups in the meta-position, whilst the ammonium nitrogen atom is represented as remaining quinquevalent after the removal of acid.

Corresponding with these formulæ for free aposafranin, aposafranone must be formulated either as

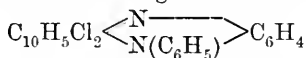


The question as to whether the ortho- or the para-quinonoid formula was the more correct aroused considerable discussion some six or seven

\* We have adopted the numbering given in Richter's *Lexikon*, whereas Ullmann describes the compound as 6-amino-2:7-dimethylacridine methiodide.

years ago, the para-quinonoid structure being defended by O. Fischer and E. Hepp (*Ber.*, 1895, 28, 2283, and 29, 361), and also by G. F. Jaubert (*Ber.*, 1896, 29, 414), whilst Nietzki regarded the safranine bases as being ortho-quinonoid, not merely in their salts, but also in the free state (*Ber.*, 1896, 29, 1445).

Kehrmann at first held an intermediate view, supposing that the aposafranine salts are ortho-quinonoid derivatives, whereas the para-quinonoid structure results when the acid is withdrawn (*Annalen*, 1896, 290, 257). Fischer and Hepp, who treated rosindone with phosphorus pentachloride, obtained phenylchloronaphthaphenazonium chloride and not a dichloride having the structure

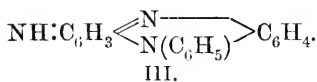
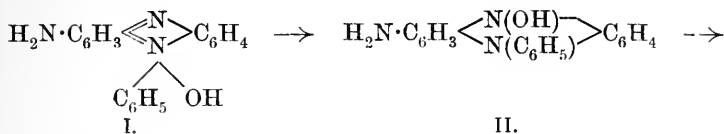


(*Ber.*, 1897, 30, 1827), but they pointed out at the same time that such an agent as phosphorus pentachloride might effect intramolecular change. Shortly afterwards, Kehrmann accepted Nietzki's view that aposafranone is an internal anhydride, but at the same time he showed that phenylphenazonium salts readily give aposafranone when treated with alkali in presence of air, or aposafranine when the alkali is replaced by ammonia (*Ber.*, 1897, 30, 2620). Fischer and Hepp subsequently (*Ber.*, 1898, 31, 299) concurred with the other investigators, with the exception of Jaubert, in accepting the ortho-quinonoid formula, and since this period aposafranone and the base, aposafranine, have generally been represented as meta-anhydrides.

One of the present authors has never accepted this view because aposafranone is practically insoluble in water and gives salts which are hydrolysed with great readiness. Were aposafranone really an internal anhydride of a phenol containing a powerful quaternary ammonium hydroxide group, then it should be comparable with the hydroxyphenyltrimethylammonium hydroxides which are readily soluble and very alkaline, and moreover give stable salts with acids.\*

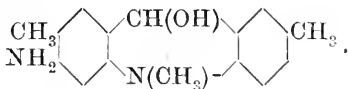
The conversion of an aposafranine salt into an anhydro-base of para-quinonoid structure is not only possible, but indeed probable, if the hydroxyl radicle of the ammonium group is assumed to migrate to the para-nitrogen atom. The product would, however, be a substituted hydroxylamine and would immediately lose the elements of water, so that the intermediate product (formula II.) in the following scheme might not be sufficiently stable to admit of isolation.

\* The examination of such hydroxides and the determination of their electrical conductivity is now being undertaken in the laboratory of the East London Technical College.—J. T. H.



If, however, the nitrogen atom of the ring were replaced by a methenyl group, the intermediate product, II., might be possible, especially since carbinol bases are produced by the action of alkalis on quaternary acridinium iodides (H. Decker, *J. pr. Chem.*, 1892, 45, 161; A. Bernthsen, *Ber.*, 1892, 25, 1746; A. Hantzsch, *Ber.*, 1899, 32, 275).

We consequently started with 3:7-dimethyl-8-acetaminoacridine (Ullmann, *Ber.*, 1903, 36, 1025), which was converted into a methiodide. By precipitating the iodide with ammonia, a carbinol base was obtained from which the acetyl group was removed by boiling with dilute sulphuric acid and reprecipitation with ammonia. The product of hydrolysis was a carbinol base,  $\text{C}_{16}\text{H}_{18}\text{ON}_2$ , which can only have the constitution



This base, when heated at about  $200^\circ$ , loses the elements of water; the resulting anhydro-base,  $\text{C}_{16}\text{H}_{16}\text{N}_2$ , redissolves in acids furnishing salts identical with those produced by the carbinol base, the hydrochloride, for example, being  $\text{C}_{16}\text{H}_{17}\text{N}_2\text{Cl}$ . It is noteworthy that the base, although containing two nitrogen atoms, is only monacidic, a property which it shares with aposafranine.

*8-Amino-3:7-dimethylacridine.*—This colouring matter has already been described by Ullmann (*Ber.*, 1903, 36, 1025), who obtained it by the action of *p*-toluidine on tetra-aminoditolylmethane. Our material was prepared by the method indicated by H. Terrisse and G. Darier (*D.R.*-P. 107,517).

The methylene derivative of *m*-tolylenediamine, obtained by the action of 40 per cent. formaldehyde solution on this diamine suspended in water, was dissolved in six parts by weight of fused *p*-toluidine, three parts of *p*-toluidine hydrochloride being then added and the mixture heated for 3 hours at  $160^\circ$ . The excess of *p*-toluidine was then removed in a current of steam, the residue was digested with hot water, the extract filtered after cooling, and the sparingly soluble nitrate of the base precipitated by the addition of potassium nitrate.

The base, which was liberated from this salt by ammonia, was dried and extracted with toluene. The residue usually melted above  $240^{\circ}$ , whilst the purified colouring matter, after recrystallising from alcohol, melted at  $245^{\circ}$  (compare Terrisse and Darier).

The acetylation was carried out according to Ullmann's method; but the melting point of our product was somewhat higher than that given by this investigator.

The acetylated base was heated in a sealed tube for 4 hours at  $110\text{--}120^{\circ}$  with five times its weight of methyl alcohol and one and a half molecular proportions of methyl iodide. The methyl-alcoholic solution was filtered and allowed to crystallise; the salt, which separated in small, very dark needles, was fairly soluble in water, the solubility being comparable with that of acridinium methiodide; it had no definite melting point.

0.1166 gave 0.0671 AgI.  $I = 31.1$ .

$C_{18}H_{19}ON_2I$  requires  $I = 31.3$  per cent.

*8-Amino-5-hydroxy-3:7:10-trimethyldihydroacridine*.—A solution of the foregoing methiodide, when left in contact with dilute ammonia, did not yield a carbinol base corresponding with the acetamino-compound owing to the ease with which the acetyl group was hydrolysed. The precipitate was therefore collected, washed, and boiled for 3 or 4 hours with 25 per cent. sulphuric acid to ensure the complete hydrolysis of the acetamino-group. The filtered dark-red solution was then poured into ammonia solution, the precipitate being dried in the air and extracted with dry acetone. After the addition of benzene, the extract was allowed to evaporate slowly, when pale reddish, microscopic needles were obtained; these appeared to melt at  $210^{\circ}$ , but in all probability the apparent melting was really nothing more than the removal of the elements of water.

0.0879 gave 0.2434  $CO_2$  and 0.0572  $H_2O$ .  $C = 75.5$ ;  $H = 7.3$ .

0.1209 „ 11.9 c.c. nitrogen at  $18.5^{\circ}$  and 763 mm.  $N = 11.3$ .

$C_{16}H_{18}ON_2$  requires  $C = 75.6$ ;  $H = 7.1$ ;  $N = 11.0$  per cent.

On keeping this substance, it darkens considerably; this change may be due either to a gradual oxidation resulting in an acridone, or possibly to the removal of the elements of water. The carbinol dissolves readily in acetone and the alcohols, is somewhat soluble in benzene, but practically insoluble in petroleum. The solutions of this substance darken very considerably on the addition of acids.

The first attempts to remove the elements of water were made by heating the dry substance in a bath of aniline vapour at  $184^{\circ}$ . The product, although much darker, did not give analytical numbers agreeing with those required for the formula  $C_{16}H_{16}N_2$ . We therefore

resorted to the following method, by means of which the desired result was obtained. A solution of this substance in nitrobenzene was heated for several hours just below the boiling point of the solvent. The liberation of water was rendered very evident by the crackling sound produced; eventually, the hot solution was filtered, and when cold treated with excess of light petroleum. The dark red precipitate produced was collected, washed with light petroleum, and dried.

Analysis of this substance proved conclusively that one molecule of water had been removed from the carbinol base.

0.1138 gave 0.3370  $\text{CO}_2$  and 0.0702  $\text{H}_2\text{O}$ .  $\text{C} = 80.8$ ;  $\text{H} = 6.9$ .

0.1062 „ 10.8 c.c. nitrogen at  $15^\circ$  and 769 mm.  $\text{N} = 12.0$ .

$\text{C}_{16}\text{H}_{16}\text{N}_2$  requires  $\text{C} = 81.3$ ;  $\text{H} = 6.8$ ;  $\text{N} = 11.9$  per cent.

The anhydro-base did not melt below  $250^\circ$ , and for this reason we think that the ill-defined melting point ( $210^\circ$ ) observed in the case of the carbinol base is not really caused by fusion, but rather by the removal of the elements of water.

This anhydro-base differs markedly from the carbinol in that it is practically insoluble in acetone or benzene, although its solutions in acids are identical in colour with those of the latter base.

A solution of the carbinol base in excess of hydrochloric acid was evaporated on the water-bath, the resulting crystals being recrystallised. The intensely dark red salt thus obtained showed that the base was apparently monacidic towards hydrochloric acid.

0.1150 gave 0.0609  $\text{AgCl}$ .  $\text{Cl} = 13.1$ .

0.1332 „ 0.0728  $\text{AgCl}$ .  $\text{Cl} = 13.5$ .

$\text{C}_{16}\text{H}_{17}\text{N}_2\text{Cl}$  requires  $\text{Cl} = 13.0$  per cent.

This salt is easily soluble in water to a dark red solution.

Our thanks are due to the Government Grant Committee of the Royal Society for financial assistance in carrying out this work.

EAST LONDON TECHNICAL COLLEGE.

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# LV.—*The Acid Esters of Methyl Substituted Succinic Acids.*

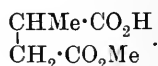
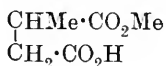
By WILLIAM ARTHUR BONE, JOHN JOSEPH SUDBOROUGH, and  
CHARLES HENRY GRAHAM SPRANKLING.

IN this communication are recorded the results of a systematic study of the methyl hydrogen esters of succinic acid and its methyl derivatives. Throughout the work, we have mainly concerned ourselves with the following questions, namely, (1) the methods of preparation, and, in the case of acids of unsymmetrical configuration, the isolation of the two possible acid esters, (2) the influence of successive methyl substitutions on the dissociation and esterification constants of the series, and (3) whether the ratio between the dissociation constants of an acid and its methyl hydrogen ester remains constant or changes in any regular manner throughout the series.

The three principal methods available for the preparation of the methyl hydrogen esters of a dibasic acid are: (1) digestion of the acidic anhydride with a slight excess of methyl alcohol, (2) partial hydrolysis of the dimethyl ester with the calculated quantity of methyl-alcoholic potash, and (3) partial esterification of the acid by the aid of a dilute solution of hydrogen chloride in methyl alcohol. Besides these three processes we also intended to employ a fourth method, namely, the action of methyl iodide on the silver hydrogen salts of the acids, but all attempts to obtain such salts entirely failed.

In the case of the symmetrical acids of the group, namely, succinic acid itself and its *s*-dimethyl and tetramethyl derivatives, we adopted the first of the three foregoing methods as the surest means of obtaining the acid ester in a state of purity. All these esters were solids at the ordinary temperature, and, except in the case of methyl hydrogen *cis*-*s*-dimethylsuccinate, we experienced no difficulty in purifying them by recrystallisation from suitable solvents.

Acids of unsymmetrical structure, for example, methyl-, *as*-dimethyl-, and trimethyl-succinic acids, should yield two isomeric methyl hydrogen esters, as represented by the following formulæ for the esters of the monomethyl acid:

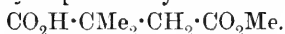


In these cases, we employed all three methods of preparation with varying degrees of success, in so far as the isolation of distinct isomeric acid esters was concerned.

The study of the dissociation and esterification constants of the

oily esters obtained from methylsuccinic acid left no doubt as to the identity of the products yielded by the three methods, but whether each product was a single chemical substance and not a mixture of isomeric esters having almost identical physical properties is perhaps an open question. In this connection, we may recall the similar experience of Braunschweig (*J. pr. Chem.*, 1893, [ii], 47, 280, 286) with the liquid ethyl hydrogen methylsuccinates prepared respectively from the acid anhydride and by partial hydrolysis of the neutral ester. The two oils had almost identical boiling points, densities, and refractive indices, yet he did not feel justified in pronouncing either of them to be a single substance. The case of methylsuccinic acid is, in this respect, paralleled by that of *cis*- $\alpha$ -methyltricarballic acid, which yields identical methyl dihydrogen esters by the three general methods (Bone and Sprankling, *Trans.*, 1902, 81, 38).

We have succeeded in obtaining two distinct crystalline methyl hydrogen *as*-dimethylsuccinates. The  $\alpha^*$ -compound, prepared either from the acid anhydride or by the partial esterification of the acid, melts at  $52^\circ$ , and has a dissociation constant  $K = 0.00228$ ; its constitution is undoubtedly expressed by the formula



The  $b^*$ -isomeride, obtained by the partial hydrolysis of the normal ester, melts at  $40.5^\circ$ , has a dissociation constant  $K = 0.00256$ , and is esterified about six times as rapidly as the  $\alpha$ -compound, a circumstance which is in complete accord with the formula  $\text{CO}_2\text{Me} \cdot \text{CMe}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ .

In his numerous experiments on acid esters of unsymmetrical acids, Wegscheider has usually found that the product yielded by any one of the three methods we have employed is really a mixture of the two isomeric esters which is difficult to separate. In the preparation of these methyl hydrogen *as*-dimethylsuccinates, we have never been able to isolate two esters in any one of the processes described; the product was always an oil which gradually deposited crystals of either  $\alpha$ - or  $b$ -compound according to the method employed. It is true that the proportion of the oil which crystallised was usually small, but the dissociation and esterification constants of the

\* With regard to the nomenclature of such isomeric acid esters, we have, in this paper, followed the recent example of workers on the Continent in adopting Wegscheider's system (*Ber.*, 1902, 35, 4330), according to which the ester having the smaller electrical conductivity is called the  $\alpha$ -ester and the other the  $b$ -ester, rather from a desire to avoid confusion of terms than from a conviction that no better system can be devised. On the contrary, we would prefer the suggestion made by one of us (*Proc.*, 1901, 17, 43) that the nomenclature should be based on the esterification constants rather than on the electrical conductivities, since results already obtained in the acetic and benzoic series indicate that the esterification velocity of an acid is more simply related to its constitution than is the electrical conductivity.

residual oil were always only slightly different from the corresponding values obtained from the crystals which had separated.

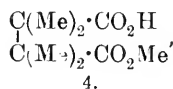
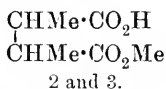
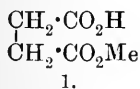
The methyl hydrogen esters of trimethylsuccinic acid have presented great difficulties; the products yielded by all three methods were oils which, on distillation under 20—30 mm. pressure, dissociated more or less completely into the acid anhydride and methyl alcohol. In order to purify these oils, they were dissolved in sodium carbonate and the neutral impurities extracted with ether. The alkaline liquid was subsequently acidified with a slight excess of hydrochloric acid, and the liberated methyl hydrogen ester extracted with light petroleum (b. p. 30—40°), a solvent which has no action on trimethylsuccinic acid itself. We never succeeded in obtaining crystals from any of the purified oils, but the values obtained for both dissociation and esterification constants indicated that, as in the case of *as*-dimethylsuccinic acid, the acid esters obtained from the anhydride and by the partial esterification of the acid are identical and different from the product of the partial hydrolysis of the normal ester.

A noteworthy property of all these methyl hydrogen succinates is their great stability in presence of water at the ordinary temperature. Thus, for example, methyl hydrogen succinate was not appreciably hydrolysed by cold water in 5 days, and methyl hydrogen methylsuccinate was not affected in 11 days.

The retarding influence produced by the introduction of various substituents on the rate of esterification of an organic acid has already been proved in several series of acids. Thus in the benzoic series a single ortho-substituent produces considerable retardation, and two ortho-substituents as a rule produce total inhibition (Meyer and Sudborough, *Ber.*, 1894, 27, 510, 1580, 3146; Lepsius, *ibid.*, 1635; V. Meyer, *Ber.*, 1895, 28, 182, 1254, 2773, 3196; 1896, 29, 830, 1397; van Loon and V. Meyer, *Ber.*, 1896, 29, 839; Goldschmidt, *Ber.*, 1895, 28, 3218; Kellas, *Zeit. physikal. Chem.*, 1897, 24, 221). The successive substitution of the three hydrogen atoms of acetic acid by other groups, no matter whether positive or negative in character, always produces retardation when the usual catalytic method of esterification is employed (Sudborough and Lloyd, *Trans.*, 1899, 75, 467). In the acrylic series, the retarding influences of  $\alpha$ -substituents, as well as the relative effects of *cis*- and *trans*-positions with respect to the carboxyl group, have been investigated (Sudborough and Lloyd, *Trans.*, 1898, 73, 81).

The catalytic method for the determination of esterification constants has already been fully described (*Trans.*, 1899, 75, 471), but since it is only applicable to monobasic acids it was necessary, when we wished to extend the observations to the succinic series, to examine the methyl hydrogen esters.

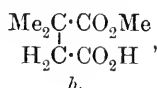
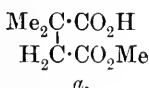
The results of experiments with the methyl hydrogen esters of the three symmetrical succinic acids afford another remarkable example of the retardation induced by the successive introduction of methyl groups. Thus, of the four compounds:



*cis*- and *trans*-Modifications.

the first is esterified very readily at 15°, when *N*/80 hydrogen chloride is employed as the catalytic agent, the process being almost completed in a few hours. With compound No. 4, the process is so very slow, even when *N*/40 hydrogen chloride is used, that no definite constant could be obtained. Compounds 2 and 3 are intermediate in this respect between 1 and 4, and the *cis*-compound is esterified more readily than its *trans*-isomeride.

Then, again, we find that methyl hydrogen succinate is esterified more than twice as rapidly as methyl hydrogen methylsuccinate; moreover, of the two methyl hydrogen *as*-dimethylsuccinates:



the *b*-compound is esterified about six times as rapidly as the *a*-ester, whilst the esterification velocity of the latter is considerably greater than that of either of the methyl hydrogen trimethylsuccinates.

A comparison of the values of  $E_{\text{MeOH}}^{15}$  (esterification constant) and  $K$  (dissociation constant) tabulated on page 540 shows that there is no connection between the two sets of numbers, or, in other words, that the esterification velocity, when the catalytic method is employed, is independent of the strength of the acidic group. A similar fact was observed in the acetic series (Sudborough and Lloyd, *Trans.*, 1899, 75, 480). But since the value for  $K$  depends on the degree of ionisation in aqueous solution, whereas the values of  $E_{\text{MeOH}}^{15}$  were deduced from observations on methyl-alcoholic solutions, the two sets of numbers are perhaps scarcely comparable.

The dissociation constants of a number of ethyl hydrogen esters of dicarboxylic acids were determined by J. Walker (*Trans.*, 1892, 61, 708), who summarised his results in the following empirical rule: "the constant of the dihydrogen salt is in general from 2 to 2.5 times as great as the constant of the corresponding ethyl hydrogen salt. The only exceptions to this rule are formed by dibasic acids, the constants of which are very high, greater than 0.1." Our results indicate that this rule is not obeyed in the succinic series; the ratio,

$K$  acid/ $K$  acid ester, appears to depend largely on the number of substituent alkyl groups present, increasing from 2.12 for succinic acid to 27.0 for tetramethylsuccinic acid.

Wegscheider (*Monatsh.*, 1895, 16, 153; 1902, 23, 346) represents the dissociation constant of an unsymmetrical dicarboxylic acid which does not show dibasic dissociation at moderate dilutions as a factor  $a$  of the sum of the constants of its  $\alpha$ - and  $\beta$ -methyl hydrogen esters ( $k_a$  and  $k_b$  respectively), thus:

$$aK = k_a + k_b.$$

In the special case of a symmetrical acid, the expression becomes

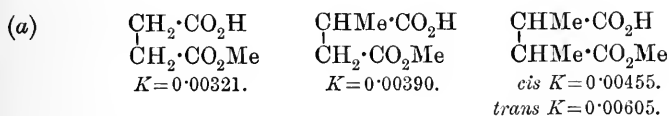
$$aK = 2k.$$

He finds that the value of  $a$  generally varies between 0.5 and 1.5, but is independent of the strength of the acid.

In a given series of dibasic acids, this factor will vary in inverse ratio to the mutual reinforcing effects of the two carboxyl groups, and it may be regarded as an index of the distances between them. In the methylsuccinate series, we find that  $a$  diminishes with successive substitutions, at first slowly, but afterwards very rapidly. Thus, whereas the value for succinic acid itself is 0.945, for the monomethyl acid it is 0.910. The second substitution lowers the factor to between 0.60 and 0.73, according to the position of the second methyl, the third substitution to 0.180, and the fourth to 0.074 (see table of properties on p. 540). Hence we may reasonably conclude that the distances between the two carboxyl groups of succinic acid diminish with successive alkyl substitutions, and that this diminution is most marked between the second and third replacements.

Further, since  $a$  for succinic acid nearly approaches unity, we may conclude that the negative character of the  $-\text{CO}_2\cdot\text{CH}_3$  group in this series of acids is not very marked. In a previous paper (Bone and Sprankling, *Trans.*, 1900, 77, 1307), it was pointed out that the magnitude of the dissociation constant in the succinic series depends on three factors, namely, (1) the number of substituent alkyl groups, (2) their mass and structure, and (3) the distances between the two carboxyl groups. The influence of the second factor was deduced from a comparison of the constants of a large number of alkylsuccinic acids. It was, however, impossible to distinguish between the effects of the first and third factors, or, in other words, between the direct and indirect effects of successive alkyl substitutions. Now, however, that the constants of the whole series of methyl hydrogen methylsuccinates have been determined, we are in a position to judge of the direct effects of methyl substitutions. Our experiments warrant the two following conclusions:

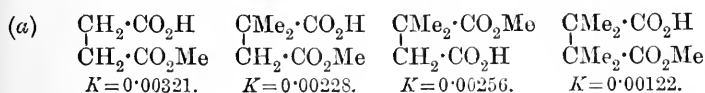
I. A single substitution of hydrogen by methyl in the group  $H_2\dot{C}\cdot CO_2H$  or  $H_2\dot{C}\cdot CO_2Me$  always raises the dissociation constant. Thus we have :



(b) Methyl hydrogen *as*-dimethylsuccinate from anhydride,  $K=0\cdot00228$ .

Methyl hydrogen trimethylsuccinate from anhydride,  $K=0\cdot00310$ .

II. On the other hand, a double substitution of methyl in the group  $H_2\dot{C}\cdot CO_2H$  or  $H_2\dot{C}\cdot CO_2Me$  involves a marked lowering of the constant, as, for example :



		$K$ .
(b)	Methyl hydrogen methylsuccinate.....	0.00390
	„ „ trimethylsuccinate.....	{ 0.00310
		0.00266

The properties of the methyl hydrogen succinates are shown in the table on p. 540.

# EXPERIMENTAL.

## 1. Methyl Hydrogen Succinate, $CO_2H\cdot CH_2\cdot CH_2\cdot CO_2Me$ .

This acid ester has already been prepared by J. Walker (Trans., 1892, 61, 716). The method we adopted was as follows : 5 grams of succinic anhydride were boiled in a reflux apparatus for 45 minutes with twice the theoretical amount of pure methyl alcohol, the excess of alcohol was removed, and the residue crystallised from hot carbon disulphide. A small amount of insoluble material, melting at  $185^\circ$  and presumably succinic acid, was obtained together with an almost theoretical yield of the acid ester in the form of glistening, white plates melting at  $58^\circ$ .

In the case of these acid esters, we find that an analysis of the silver salt, or the titration of the ester itself with standard barium hydroxide, using phenolphthalein as indicator, is a more delicate test of purity than the estimation of carbon and hydrogen by the usual combustion method.

0.2492 silver salt gave 0.1132 Ag.  $Ag=45\cdot4$ .

$C_5H_7O_4Ag$  requires  $Ag=45\cdot2$  per cent.

Methyl hydrogen ester of	Prepared from	Melting point.	Esterification constant, $P_{H_2O}^{15}$	Dissociation constant, $K$ .	$K$ for original acid.	$K$ -acid ester.	$a$ in $aK = K_a + K_b$ .
Succinic .....	Anhydride	58°	17.51; 17.02	0.00321	0.00679	2.12	0.945
Methylsuccinic .....	Anhydride Neutral ester Acid	Liquid ,, ,,	6.87; 7.12	0.00390	0.00854	2.20	0.910
			6.96 7.16	0.00385 0.00380			
cis-s-Dimethylsuccinic .....	Anhydride	38°	1.47; 1.37; 1.40	0.00455	0.0124	2.73	0.734
trans-s-Dimethylsuccinic .....	Anhydride	49	0.788; 0.780	0.00605	0.0196	3.07	0.617
αs-Dimethylsuccinic .....	Anhydride Neutral ester Acid	52	0.261; 0.276	0.00228	0.00805	3.50	0.604
		40.5 52.0	1.78; 1.75 0.280	0.00256 0.00230		3.15 3.50	
Trimethylsuccinic .....	Anhydride Neutral ester Acid	Liquid	0.085; 0.083	0.00310	0.0321	10.30	0.180
		,, ,,	0.128; 0.118 0.086; 0.085	0.00266 0.00312		12.0 10.30	
Tetramethylsuccinic .....	Anhydride	63°	Too small to be measured	0.00122	0.0330	27.0	0.074

0.1651 and 0.33 required 25 and 50 c.c.  $N/20$   $\text{Ba}(\text{OH})_2$  respectively, the amounts coinciding with the calculated quantities.

As Braunschweig (*J. pr. Chem.*, 1893, [ii], 47, 279) states that methyl hydrogen methylsuccinate is readily hydrolysed when left in contact with water for a short time, we have examined the action of water at the ordinary temperature on methyl hydrogen succinate, but have found that even after 5 days no appreciable hydrolysis occurs: 1.98 grams of the acid ester were made up to 150 c.c. with distilled water and 15 c.c. of the solution were titrated at given intervals with standard barium hydroxide, using phenolphthalein as indicator.

Time in hours.....	0	1	2	20	43	115
$N/20$ $\text{Ba}(\text{OH})_2$ in c.c. ....	30.1	30.1	30.1	30.1	30.0	30.1

*Electrical Conductivity.*  $\mu_\infty = 354$ .

$v$ .	$\mu_v$ .	$m$ .	100k.
17.9	8.33	0.0235	0.00316
35.8	11.88	0.0335	0.00324
71.6	16.71	0.0472	0.00327
143.2	23.09	0.0652	0.00317

Mean = 0.00321

This agrees very well with the value  $K = 0.00326$ , obtained by Walker (*loc. cit.*).

#### *Esterification Constant.\**

A. 15 c.c. of the alcoholic solution required 30.0 c.c. of  $N/20$   $\text{Ba}(\text{OH})_2$ .

$t$ in hours.	$a - x$ .	$1/t \log a/a - x$ .
1	24.1	0.0951
2	19.4	0.0947
3	15.6	0.0947
4	12.6	0.0942

Strength of  $\text{HCl} = N/80$ .

B. 15 c.c. of the alcoholic solution required 29.8 c.c. of  $N/19.9$   $\text{Ba}(\text{OH})_2$ .

$t$ in hours.	$a - x$ .	$1/t \log a/a - x$ .
1	23.8	0.0976
2	19.15	0.0960
3	15.5	0.0946
4	12.5	0.0943

Strength of  $\text{HCl} = N/80$ .

Mean of A and B = 0.0951.

$$E_{\text{MeOH}}^{15^\circ} = 0.0951 \times 80 \times 2.3026 = 17.51.$$

\* The method employed was similar to that previously described (Abstr., 1899, 75, 471). An  $N/10$  solution of the acid ester was prepared and 15 c.c. were carefully titrated with standard barium hydroxide. A given volume (usually 70 c.c.) of this solution was mixed with an equal volume of standard hydrogen chloride in pure methyl alcohol. Quantities of 30 c.c. of the mixture were introduced into separate small bottles, placed in a thermostat at  $15^\circ$ , and titrated after given intervals of time with the standard barium hydroxide.

C. 15 c.c. of the alcoholic solution required 30.7 c.c. of  $N/20$

$Ba(OH)_2$ .

$t$ in hours.	$a-x$ .	$1/t \log a/a-x$ .
1	24.7	0.0944
1.5	22.5	0.0900
2.5	18.0	0.0927
3.5	14.6	0.0922

Mean = 0.0923.

HCl =  $N/80$ .

$$E_{MeOH}^{15} = 0.0928 \times 80 \times 2.3026 = 17.02.$$

D. 15 c.c. of the alcoholic solution required 30.15 c.c. of  $N/20$

$Ba(OH)_2$ .

$t$ in hours.	$a-x$ .	$1/t \log a/a-x$ .
1	24.2	0.0955
2	19.65	0.0930
2.5	17.6	0.0935
3	15.95	0.0922

Mean = 0.0936.

HCl =  $N/78.9$ .

$$E_{MeOH}^{15} = 17.01.$$

## 2. Methyl Hydrogen Methylsuccinate.

### (a) From Anhydride.

The anhydride was prepared by heating the acid with excess of acetyl chloride for 2 hours; it distilled at 238—240° (uncorr.) under atmospheric pressure, slowly solidified to a crystalline mass melting at 30—32°, and when washed with cold carbon disulphide melted at 37°. Thirty grams of the anhydride were boiled with 10 grams of anhydrous methyl alcohol for an hour and the product distilled under diminished pressure; after two fractionations, an 80 per cent. yield of an oil distilling at 140° under 11 mm. pressure was obtained. The oil dissolved readily in the ordinary solvents, including water.

0.1574 gave 0.0671 Ag. Ag = 42.7.

$C_6H_9O_4Ag$  requires 42.7 per cent.

0.201 required 27.53 c.c. of  $N/20 Ba(OH)_2$ , the calculated value being 27.53 c.c.

A weighed amount of the acid methyl ester (1.3458 grams) was made up to 150 c.c. with distilled water and 15 c.c. of the solution titrated at given intervals.

1. $t$ in hours.....	0	1	30	48	72	384	600	
$N/20 Ba(OH)_2$ in c.c....	18.5	18.5	18.6	18.5	18.5	18.9	19.1	
2.153 grams made up to 150 c.c. with water and 15 c.c. titrated.								
2. $t$ in hours .....	0	22	46	72	96	119	216	264
$N/20 Ba(OH)_2$ in c.c.	24.7	24.65	24.65	24.65	24.7	24.7	24.7	24.7

The results indicate that the ester is not so readily hydrolysed by water as stated by Braunschweig.

*Electrical Conductivity at 25°.  $\mu_{\infty} = 353$ .*

<i>v.</i>	$\mu_v$	<i>m.</i>	100 <i>k.</i>
21.2	10.01	0.0284	0.00391
42.4	14.07	0.0399	0.00391
84.8	19.67	0.0577	0.00388
169.6	27.62	0.0782	0.00391

$$K = 0.00390$$

*Esterification Constant.*

*A.* 15 c.c. of the alcoholic solution required 30.3 c.c. of *N*/20

Ba(OH)<sub>2</sub>.

<i>t</i> in hours.	<i>a</i> - <i>x.</i>	1/ <i>t</i> log <i>a</i> / <i>a</i> - <i>x.</i>
2.25	24.8	0.0387
3.25	22.9	0.0374
4.25	21.0	0.0375
5.25	19.3	0.0373
6.0	18.4	0.0361
6.5	17.5	0.0367

$$\text{Mean} = 0.0373.$$

$$\text{HCl} = N/80.$$

$$E_{\text{MeOH}}^{15^\circ} = 6.87.$$

*B.* 15 c.c. of the alcoholic solution required 29.45 c.c. of

Ba(OH)<sub>2</sub>.

<i>t</i> in hours.	<i>a</i> - <i>x.</i>	1/ <i>t</i> log <i>a</i> / <i>a</i> - <i>x.</i>
2	24.45	0.0403
4	20.45	0.0396
6	16.65	0.0412
8	14.35	0.0390

$$\text{Mean} = 0.400.$$

$$\text{HCl} = N/77.3.$$

$$E_{\text{MeOH}}^{15^\circ} = 7.12.$$

*(b) From the Normal Methyl Ester.*

Dimethyl methylsuccinate was prepared by boiling the acid with a 3 per cent. solution of hydrogen chloride in pure methyl alcohol for 3—4 hours. The product was distilled under reduced pressure and the fraction boiling at 115—125° under 46 mm. pressure collected separately. On distillation under atmospheric pressure, the ester was obtained as a colourless oil boiling at 197—198°.

A mixture of 26 grams of the normal ester and 20 grams of methyl alcohol was treated with 63.2 grams of a 14.4 per cent. solution of potassium hydroxide in pure methyl alcohol, and the whole kept for 5 hours. A little solid methyl-orange was added and hydrogen chloride passed into the liquid until a permanent pink coloration was produced. The potassium chloride was removed and the liquid distilled under reduced pressure. A certain amount of oil distilling below 120° under 15 mm. pressure was obtained and found to consist of unaltered normal ester. The fraction boiling at 135—150° was collected separately and rectified, the portion distilling at 142—143° under 15 mm. pressure being collected and analysed. A substance with a higher

boiling point was left in the flask and partially solidified on cooling. The yield of acid ester was about 25 per cent.

0.2135 gave 0.091 Ag.  $\text{Ag} = 42.6$ .

$\text{C}_6\text{H}_9\text{O}_4\text{Ag}$  requires  $\text{Ag} = 42.7$  per cent.

*Electrical Conductivity at 25°.  $\mu_\infty = 353$ .*

v.	$\mu_v$	m.	100k.
16.89	8.92	0.0253	0.00389
33.78	12.49	0.0354	0.00385
67.56	17.45	0.0494	0.00380
135.12	24.60	0.0697	0.00387

$$K = 0.00385.$$

*Esterification Constant.*

A. 15 c.c. of the alcoholic solution required 30.7 c.c. of  $N/20$

$\text{Ba(OH)}_2$ .

t in hours.	a - x.	$1/t \log a/a - x$ .
2	25.7	0.0386
4	21.5	0.0387
5	19.9	0.0376
6	18.3	0.0374
6.5	17.7	0.0368
8.5	15.0	0.0366

B. 15 c.c. of the alcoholic solution required 30.75 c.c. of  $N/20$

$\text{Ba(OH)}_2$ .

t.	a - x.	$1/t \log a/a - x$ .
2	25.7	0.0390
4	21.6	0.0383
5.5	18.9	0.0373
8	15.6	0.0368

Mean of A and B = 0.0378;  $\text{HCl} = N/80$ .

$$E_{\text{MeOH}}^{15^\circ} = 6.96.$$

(c) *By Partial Esterification of Methylsuccinic Acid.*

Twenty-five grams of the acid were boiled for half an hour with 45 c.c. of a  $N/10$  methyl-alcoholic solution of hydrogen chloride, and the product fractionated under reduced pressure; the portion distilling at  $130\text{--}140^\circ$  was again fractionated and ultimately 8 grams of oil distilling at  $138\text{--}140^\circ$  under 13 mm. pressure were obtained.

0.2065 gave 0.0885 Ag.  $\text{Ag} = 42.8$ .

$\text{C}_6\text{H}_9\text{O}_4\text{Ag}$  requires  $\text{Ag} = 42.7$  per cent.

*Electrical Conductivity at 25°.  $\mu_\infty = 353$ .*

v.	$\mu_v$	m.	100k.
6.0	5.23	0.0148	0.00371
12.0	7.56	0.0214	0.00390
24.0	10.50	0.0297	0.00380
48.0	14.74	0.0417	0.00380

$$K = 0.00380.$$

*Esterification Constant.*

A. 15 c.c. of the alcoholic solution required 30.4 c.c of  $N/20$   $\text{Ba}(\text{OH})_2$ .

$t.$	$a-x.$	$1/\log a/a-x.$
2	25.5	0.0382
3	23.1	0.0397
4.5	20.2	0.0394
6	18.0	0.0379
7	16.2	0.0391

Mean = 0.0389 ;  $\text{HCl} = N/80$ .

$$E_{\text{MeOH}}^{15^\circ} = 7.16.$$

*3. Methyl Hydrogen cis-s-Dimethylsuccinate.*

Ten grams of the anhydride were boiled in a reflux apparatus with twice the theoretical amount of pure methyl alcohol during 4 hours. The mixture, when kept in a desiccator over sulphuric acid, ultimately solidified ; as it was so readily soluble in all ordinary solvents, it was merely dissolved in cold light petroleum ( $30-40^\circ$ ), and when the solvent was removed an oil was obtained which gradually set to a mass of large, colourless, transparent prisms melting at  $38^\circ$ .

0.207 gave 0.0843 Ag.  $\text{Ag} = 40.7$ .

$\text{C}_7\text{H}_{11}\text{O}_4\text{Ag}$  requires  $\text{Ag} = 40.45$  per cent.

0.2 gram of ester required 25 c.c. of  $N/19.72$   $\text{Ba}(\text{OH})_2$ , the calculated value being 24.65 c.c.

The ester was evidently not quite pure and contained a small amount of anhydride or acid.

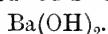
*Electrical Conductivity at  $25^\circ$ .  $\mu_\infty = 352$ .*

$v.$	$\mu_v.$	$m.$	100 $k.$
21.97	11.09	0.0315	0.00466
43.94	15.15	0.0430	0.00440
87.88	21.89	0.0622	0.00469
175.76	29.81	0.0847	0.00446

$$K = 0.00455.$$

*Esterification Constant.*

A. 15 c.c. of the alcoholic solution required 31.2 c.c. of  $N/20$



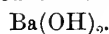
$t.$	$a-x.$	$1/t \log a/a-x.$
4	23.1	0.0326
6	19.8	0.0329
7	18.4	0.0328
10	14.9	0.0321

Mean = 0.0326.

HCl =  $N/19.6$ .

$E_{\text{MeOH}}^{15^\circ} = 1.47$ .

B. 15 c.c. of the alcohol solution required 31.35 c.c. of  $N/20$



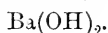
$t.$	$a-x.$	$1/t \log a/a-x.$
3	25.2	0.0316
6	20.9	0.0293
8	18.3	0.0292
10	16.1	0.0289

Mean = 0.0297.

HCl =  $N/20$ .

$E_{\text{MeOH}}^{15^\circ} = 1.37$ .

C. 15 c.c. of the alcoholic solution required 30.37 c.c. of  $N/20$



$t.$	$a-x.$	$1/t \log a/a-x.$
2	26.40	0.0304
4	22.95	0.0304
5.5	20.45	0.0312
7	18.70	0.0301

Mean = 0.0305.

HCl =  $N/20$ .

$E_{\text{MeOH}}^{15^\circ} = 1.40$ .

#### 4. Methyl Hydrogen trans-s-Dimethylsuccinate.

This ester was prepared in exactly the same manner as the isomeric *cis*-ester, and the solid obtained was crystallised from light petroleum (b. p. 30—40°). It separates in colourless plates, melts at 49°, is readily soluble in most organic solvents, and may be distilled under reduced pressure.

0.1466 gave 0.2834  $\text{CO}_2$  and 0.1009  $\text{H}_2\text{O}$ .  $\text{C} = 52.72$ ;  $\text{H} = 7.64$ .

$\text{C}_7\text{H}_{12}\text{O}_4$  requires  $\text{C} = 52.50$ ;  $\text{H} = 7.50$  per cent.

The *silver* salt crystallises in small needles and is moderately soluble in water.

0.1406 gave 0.0572 Ag.  $\text{Ag} = 40.7$ .

$\text{C}_7\text{H}_{11}\text{O}_4\text{Ag}$  requires  $\text{Ag} = 40.45$  per cent.

0.2 gram of the ester required 24.7 c.c. of  $N/19.72$   $\text{Ba(OH)}_2$  for neutralisation, using phenolphthalein as indicator, the calculated value being 24.65 c.c.

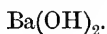
*Electrical Conductivity at 25°.  $\mu_{\infty} = 352$ .*

$\%$	$\mu_v$	$m$	100k.
34.48	15.51	0.0441	0.00590
68.96	21.99	0.0625	0.00604
137.92	30.81	0.0875	0.00609
275.84	42.84	0.1220	0.00615

$$K = 0.00605.$$

*Esterification Constant.*

A. 15 c.c. of the alcoholic solution required 31.2 c.c. of  $N/20$



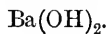
$t$	$a-x$	$1/t \log a/a-x$
14	27.0	0.00448
24	24.6	0.00430
38	21.4	0.00431
48	19.6	0.00421
61	17.3	0.00420
67	16.3	0.00421

$$\text{Mean} = 0.00428.$$

$$\text{HCl} = N/80.$$

$$E_{\text{MeOH}}^{15^\circ} = 0.788.$$

B. 15 c.c. of the alcoholic solution required 24 c.c. of  $N/19.72$



$t$	$a-x$	$1/t \log a/a-x$
12	21.3	0.00432
24	19.0	0.00423
36	16.8	0.00431

$$\text{Mean} = 0.00429.$$

$$\text{HCl} = N/78.9.$$

$$E_{\text{MeOH}}^{15^\circ} = 0.780.$$

5. *Methyl, Hydrogen as-Dimethylsuccinate.*

(a) *From the Anhydride.*

The ester was prepared by the method already described for the *cis*- and *trans*-esters. The oil obtained when the excess of alcohol was evaporated, yielded in the course of two or three days a considerable quantity of large, flat plates. When recrystallised from light petroleum (b. p. 40—60°), the ester forms well developed, colourless prisms, melting at 52°.

0.1871 gave 0.3605  $\text{CO}_2$  and 0.1279  $\text{H}_2\text{O}$ .  $\text{C} = 52.55$ ;  $\text{H} = 7.59$ .

$\text{C}_7\text{H}_{12}\text{O}_4$  requires  $\text{C} = 52.5$ ;  $\text{H} = 7.50$  per cent.

0.154 silver salt gave 0.0626 Ag.  $\text{Ag} = 40.6$ .

$\text{C}_7\text{H}_{11}\text{O}_4\text{Ag}$  requires  $\text{Ag} = 40.45$  per cent.

0.3 gram of the ester required 37.45 c.c. of  $N/20$   $\text{Ba(OH)}_2$ , the calculated value being 37.5 c.c.

*Electrical Conductivity at 25°.  $\mu_{\infty} = 352$ .*

<i>v.</i>	$\mu_v$	<i>m.</i>	100 <i>k.</i>
20.39	7.45	0.0212	0.00225
40.78	10.62	0.0302	0.00230
81.56	14.94	0.0424	0.00230
173.18	21.32	0.0606	0.00226

$$K = 0.00228.$$

*Esterification Constant.*

A. 15 c.c. of the alcoholic solution required 29.7 c.c. of *N*/19.9 | B. 15 c.c. of the alcoholic solution required 29.7 c.c. of *N*/19.72

Ba(OH) <sub>2</sub> .			Ba(OH) <sub>2</sub> .		
<i>t.</i>	<i>a</i> - <i>x.</i>	$1/t \log a/a - x.$	<i>t.</i>	<i>a</i> - <i>x.</i>	$1/t \log a/a - x.$
11.5	27.58	0.00280	16	26.62	0.00297
24	25.33	0.00288	41	22.22	0.00307
36	23.48	0.00283	64	19.1	0.00299
49	21.58	0.00283	89	16.2	0.00296
Mean = 0.00283.			Mean = 0.00300.		
HCl = <i>N</i> /40.			HCl = <i>N</i> /40.		
$E_{\text{MeOH}}^{15^\circ} = 0.261.$			$E_{\text{MeOH}}^{15^\circ} = 0.276.$		

*(b) From the Normal Methyl Ester.*

The normal ester,  $\text{CO}_2\text{Me} \cdot \text{CMe}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{Me}$ , obtained by the action of methyl iodide on the silver salt, is a colourless liquid distilling at 201—202° (uncorr.) under atmospheric pressure. For the preparation of the acid ester, 44.5 grams of the normal ester were mixed with the theoretical amount (285 c.c.) of methyl-alcoholic potash, and the mixture left overnight at the ordinary temperature. Next morning, the mixture was heated for 2 hours on the water-bath, and the alcohol then distilled off under reduced pressure. The syrupy residue was mixed with the theoretical amount of dilute hydrochloric acid, and the oily acid ester thus liberated extracted with pure ether. After drying the extract and removing the solvent, the ester was distilled under reduced pressure, when 26 grams of an oil distilling at 141° under 14 mm. pressure were obtained.

0.2967 silver salt gave 0.1213 Ag.  $\text{Ag} = 40.9$ .

$\text{C}_7\text{H}_{11}\text{O}_4\text{Ag}$  requires 40.45 per cent.

Although not quite pure, the conductivity and esterification constant of the oil were determined.

*Electrical Conductivity at 25°.  $\mu_{\infty} = 352$ .*

<i>v.</i>	$\mu_v$	<i>m.</i>	100 <i>k.</i>
11.59	5.90	0.0168	0.00248
23.18	8.54	0.0243	0.00261
46.36	12.30	0.0350	0.00275
92.72	17.25	0.0490	0.00272

$$K = 0.00264.$$

*Esterification Constant.*

15 c.c. of the alcoholic solution required 32.95 c.c. of  $N/22.16$   $\text{Ba(OH)}_2$ .

<i>t.</i>	<i>a - x.</i>	$1/t \log a/a - x.$	<i>t.</i>	<i>a - x.</i>	$1/t \log a/a - x.$
3.5	28.85	0.0165	24	15.55	0.0136
7	25.75	0.0153	27	14.40	0.0133
22	16.55	0.0136	29.5	13.45	0.0132

$$\text{Mean} = 0.0142; \text{HCl} = N/41.1.$$

$$E_{\text{MeOH}}^{15^\circ} = 1.34.$$

When kept for some time, the ester deposited large, flat plates, which were removed and crystallised from light petroleum. The amount of crystals was relatively small, being only about 7 grams from 26 grams of oil. The ester crystallised from light petroleum in snow-white, rhomboidal plates melting at  $40.5$ — $41^\circ$ . The numbers obtained for the electrical conductivity and esterification constant were very similar to those obtained for the original oil, thus proving that, although only 7 grams of the solid ester were obtained from the oil, yet the remainder must have consisted of the nearly pure ester.

0.2 gram required 25.1 c.c. of  $N/20$   $\text{Ba(OH)}_2$ , the calculated value being 25.0 c.c.

*Electrical Conductivity (of crystalline ester) at 25°.*

<i>v.</i>	$\mu_v$	<i>m.</i>	100 <i>k.</i>
27.6	9.14	0.0260	0.00252
55.2	12.91	0.0367	0.00253
110.4	18.20	0.0517	0.00255
220.8	25.80	0.0733	0.00263

$$K = 0.00256.$$

*Esterification Constant.*

A. 15 c.c. of the alcoholic solution required 30.3 c.c. of $N/19.9$ Ba(OH) <sub>2</sub> .			B. 15 c.c. of the alcoholic solution required 30 c.c. of $N/19.9$ Ba(OH) <sub>2</sub> .		
<i>t.</i>	<i>a - x.</i>	$1/t \log a/a - x.$	<i>t.</i>	<i>a - x.</i>	$1/t \log a/a - x.$
4	25.18	0.0201	3	23.0	0.0384
6	23.08	0.0197	4.5	20.2	0.0381
8.5	20.7	0.0195	5.5	18.55	0.0379
10.5	19.08	0.0191	6.5	17.0	0.0380
Mean = 0.0196; HCl = $N/39.4$ .			Mean = 0.0381; HCl = $N/19.9$ .		
$E_{MeOH}^{15^\circ} = 1.78.$			$E_{MeOH}^{15^\circ} = 1.75.$		

*(c) Acid Ester from the Acid.*

A solution of 16.5 grams of the acid melting at 140—141° in 40 c.c. of  $N/5$  methyl-alcoholic hydrogen chloride was boiled for 40 minutes in a reflux apparatus. The excess of alcohol and hydrogen chloride was removed under reduced pressure, and the residue fractionated under 14 mm. pressure. The fraction boiling below 110° gave 6 grams of the normal ester boiling at 200°, the second fraction distilling between 130° and 145° was rectified, and the portion distilling at 142—143° under 14 mm. pressure gave 4 grams of a solid, which, after crystallisation from light petroleum, melted at 52°. This ester was identical with the ester obtained from the anhydride, a mixture of the two melted at 52°, and the conductivities and esterification constants of the two were practically identical.

0.2 gram required 25.0 c.c. of  $N/20$  Ba(OH)<sub>2</sub>, the calculated value being 25.0 c.c.

*Electrical Conductivity at 25°.  $\mu_\infty \approx 352.$* 

<i>v.</i>	$\mu_v.$	<i>m.</i>	100 <i>k.</i>
25.18	8.28	0.0235	0.00225
50.36	11.84	0.0336	0.00232
100.72	16.52	0.0469	0.00230
201.44	23.22	0.0660	0.00232

$$K = 0.00230.$$

*Esterification Constant.*

Fifteen c.c. of the alcoholic solution required 30.45 c.c. of  $N/19.72$   $\text{Ba(OH)}_2$ .

$t$ .	$a-x$ .	$1/t \log a/a-x$ .
18	23.6	0.00615
30	19.9	0.00616
42	16.9	0.00609
53	14.7	0.00597

Mean = 0.00609;  $\text{HCl} = N/20$ .

$$E_{\text{MeOH}}^{15^\circ} = 0.280.$$

6. *Methyl Hydrogen Trimethylsuccinate.*(a) *From the Anhydride.*

The anhydride was prepared by distilling the pure acid under atmospheric pressure, and was obtained in the form of a solid mass melting at  $33^\circ$ . Its purity was tested by titration with standard barium hydroxide, when 0.1 gram required 28 c.c. of  $N/20$   $\text{Ba(OH)}_2$ , the calculated value being 28.1 c.c.

Fourteen grams of the anhydride were boiled with 10 grams of pure methyl alcohol in a reflux apparatus for 4 hours, when the product dissolved readily in cold sodium carbonate solution. Titration with standard barium hydroxide indicated that the acid ester was not quite pure, as 0.2194 gram required 25.65 c.c. of  $N/20$   $\text{Ba(OH)}_2$ , instead of the calculated value, namely, 25.2 c.c. When the ester was distilled under reduced pressure, methyl alcohol was eliminated, and a considerable amount of the anhydride was regenerated. The following method of purification was therefore adopted. The ester was dissolved in cold sodium carbonate solution, and any unaltered anhydride removed by extraction with ether. The alkaline liquid was acidified with dilute hydrochloric acid, and the oily ester thus precipitated extracted twice with relatively large amounts of light petroleum (b. p.  $30-60^\circ$ ). This solvent was selected instead of ether, because it does not dissolve trimethylsuccinic acid to any appreciable extent. The petroleum extract was dried, and the solvent removed. The oily product finally obtained was not quite pure, but evidently contained neither acid nor anhydride.

0.2194 gram required 24.6 c.c. of  $N/20$   $\text{Ba(OH)}_2$ , instead of the calculated value, namely, 25.2 c.c.

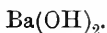
*Electrical Conductivity at 25°.  $\mu_{\infty} = 351$ .*

<i>v.</i>	$\mu_{\infty}$	<i>m.</i>	100 <i>k.</i>
17.82	7.98	0.0228	0.00300
35.64	11.57	0.0330	0.00315
71.28	16.07	0.0459	0.00310
142.56	22.42	0.0640	0.00308

$$K = 0.00310.$$

*Esterification Constant.*

A. 15 c.c. of the alcoholic solution required 28.8 c.c. of *N*/19.72



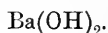
<i>t.</i>	<i>a - x.</i>	$1/t \log a/a - x.$
22	26.0	0.00201
46	23.9	0.00176
70	21.7	0.00175
94	19.7	0.00175

$$\text{Mean} = 0.00182.$$

$$\text{HCl} = \text{N}/19.76.$$

$$E_{\text{MeOH}}^{15^\circ} = 0.083.$$

B. 15 c.c. of the alcoholic solution required 30.6 c.c. of *N*/20



<i>t.</i>	<i>a - x.</i>	$1/t \log a/a - x.$
21	27.8	0.00199
46	24.9	0.00195
70	23.0	0.00177
94	21.1	0.00171

$$\text{Mean} = 0.00185.$$

$$\text{HCl} = \text{N}/19.9.$$

$$E_{\text{MeOH}}^{15^\circ} = 0.085.$$

*(b) From the Normal Ester.*

Fifteen grams of the normal ester, obtained from the silver salt, were mixed with 40 grams of 11.3 per cent. methyl-alcoholic potash and kept overnight, the mixture being then boiled for two hours and the alcohol removed under reduced pressure; the residue was dissolved in water and any normal ester removed by extraction with ether; the alkaline liquid was acidified with hydrochloric acid and then extracted twice with relatively large amounts of light petroleum. The acid ester obtained was an oil and the yield was only poor as a certain amount of the normal ester remained unaffected whilst some of the acid was liberated. The ester was purified in the manner described under the preparation of the ester from the anhydride.

0.2194 gram required 24.55 c.c. of *N*/20  $\text{Ba(OH)}_2$ , the calculated value being 25.2 c.c.

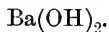
*Electrical Conductivity at 25°.  $\mu_{\infty} = 351$ .*

<i>v.</i>	$\mu_{\infty}$	<i>m.</i>	100 <i>k.</i>
18.12	7.49	0.0213	0.00256
36.24	10.80	0.0308	0.00270
72.48	15.15	0.0431	0.00268
144.96	21.34	0.0608	0.00271

$$K = 0.00266.$$

*Esterification Constant.*

A. 15 c.c. of the alcoholic solution required 36.15 c.c. of *N*/22.16



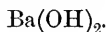
<i>t.</i>	<i>a - x.</i>	$1/t \log a/a - x.$
47	30.75	0.00149
71	28.85	0.00138
95	27.05	0.00133
119.5	25.45	0.00128
144	23.9	0.00125

$$\text{Mean} = 0.00135.$$

$$\text{HCl} = N/41.1.$$

$$E_{\text{MeOH}}^{15} = 0.128.$$

B. 15 c.c. of the alcoholic solution required 28.8 c.c. of *N*/19.9



<i>t.</i>	<i>a - x.</i>	$1/t \log a/a - x.$
23	24.9	0.00275
40	22.6	0.00263
64	19.8	0.00254
90	17.2	0.00249

$$\text{Mean} = 0.00260.$$

$$\text{HCl} = N/19.7.$$

$$E_{\text{MeOH}}^{15} = 0.118.$$

*(c) Partial Esterification of the Acid.*

Fifteen grams of trimethylsuccinic acid were dissolved in 50 c.c. of a 3 per cent. methyl-alcoholic solution of hydrogen chloride and the whole boiled for 30 minutes on the water-bath. The alcohol was removed under reduced pressure and the residue dissolved in sodium carbonate solution. Any normal ester was extracted with ether, the alkaline solution was acidified with hydrochloric acid, and the oily acid ester thus obtained extracted thrice with relatively large amounts of light petroleum, and finally the solution was extracted with ether to obtain any unaltered free acid. The amounts of normal ester, acid ester, and free acid thus obtained were 3, 7 and 3 grams respectively.

0.2010 silver salt gave 0.0780 Ag.  $\text{Ag} = 38.8.$

$\text{C}_8\text{H}_{13}\text{OAg}$  requires 38.4 per cent.

0.2 gram required 23.5 c.c. of *N*/20  $\text{Ba(OH)}_2$ , the calculated value being 23.0 c.c.

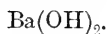
*Electrical Conductivity at 25°.  $\mu_{\infty} = 351$ .*

<i>c.</i>	$\mu_r$	<i>m.</i>	100 <i>k.</i>
42.64	12.63	0.0361	0.00317
85.28	17.65	0.0503	0.00312
170.56	24.44	0.0697	0.00308

$$K = 0.00312.$$

*Esterification Constant.*

A. 15 c.c. of the alcoholic solution required 30.9 c.c.  $N/20$



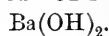
<i>t.</i>	<i>a - x.</i>	$1/t \log a/a - x.$
22	27.9	0.00202
45	25.1	0.00200
69	23.1	0.00183
80.75	22.3	0.00175
93	21.0	0.00180
117	19.4	0.00172

$$\text{Mean} = 0.00185.$$

$$\text{HCl} = N/20.2.$$

$$E_{\text{MeOH}}^{15} = 0.086.$$

B. 15 c.c. of the alcoholic solution required 32.1 c.c.  $N/20$



<i>t.</i>	<i>a - x.</i>	$1/t \log a/a - x.$
19	29.5	0.00193
42	26.7	0.00190
68	24.3	0.00178
95	22.1	0.00171

$$\text{Mean} = 0.00183.$$

$$\text{HCl} = N/20.1.$$

$$E_{\text{MeOH}}^{15} = 0.085.$$

7. *Methyl Hydrogen Tetramethylsuccinate.*

Tetramethylsuccinic acid was prepared by Meyer and Auwer's method (*Ber.*, 1890, 23, 304), and attempts were also made to obtain it by shaking a mixture of ethyl  $\alpha$ -bromoisobutyrate and finely-divided silver, but the yield was no better. The acid was transformed into anhydride by distillation under atmospheric pressure.

The acid ester was prepared by treating the anhydride (m. p. 147°) with the requisite amount of sodium methoxide dissolved in methyl alcohol, evaporating to dryness, and acidifying with hydrochloric acid; it crystallised from light petroleum (b. p. 30—40°) in the form of large, flat prisms melting at 63°, the yield being practically quantitative.

0.210 silver salt gave 0.0770 Ag.  $\text{Ag} = 36.66$ .

$\text{C}_9\text{H}_{15}\text{O}_4\text{Ag}$  requires  $\text{Ag} = 36.61$  per cent.

The silver salt is fairly readily soluble in water and forms long, felted needles.

*Electrical Conductivity at 25°.  $\mu = 350$ .*

<i>v.</i>	$\mu_v$	<i>m.</i>	100 <i>k.</i>
47.81	8.39	0.0239	0.00122
95.62	11.65	0.0333	0.00120
191.24	16.66	0.0476	0.00124
382.48	23.04	0.0658	0.00121

$$K = 0.00122.$$

The esterification constant of the acid ester could not be determined accurately as it was so very slowly transformed. Thus, when left for 144 hours in contact with *N*/40 hydrogen chloride in methyl alcohol there was only a diminution of 0.2 c.c. on titration with *N*/20 alkali.

We desire to thank the Research Fund Committee of the Society for grants which have defrayed the greater part of the expenses connected with this research.

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MANCHESTER.

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ABERYSTWYTH.

## LVI.—*Chemical Dynamics of the Alkyl Iodides.*

By KATHARINE ALICE BURKE and FREDERICK GEORGE DONNAN.

### *Introduction.*

ONE of the most important problems of modern chemistry is the investigation of the causes which give rise to the reactivity of substances. Perhaps the most interesting result of the physico-chemical researches of the last two decades has been the tracing of a connection between the chemical reactivity of salt-like substances in aqueous solution and the electrical conductivities of those solutions. The main result of these investigations may be summed up as follows. It is, in general, possible to ascribe this reactivity of salt-like substances in aqueous solution to something pre-existing in the solution and apart from the particular reaction studied. The possibility of doing this lies in the fact that this pre-existing condition or state can be qualitatively detected and quantitatively expressed by perfectly independent methods. As a consequence of this, a generalised theory of chemical reactivity has been developed. In the case, however, of organic chemistry, the great majority of substances do not possess, or, at all events, have not

as yet been shown to possess, a salt-like character, and it has not been hitherto possible—perhaps for the reason just stated—to discover any even approximately general method of measuring their reactivity. A good deal of the material with which a general theory of chemical reactivity must deal in the future, has, however, been accumulated by the accurate measurement of the velocity-coefficients of organic reactions. This, indeed, forms the only method whereby the problem can as yet be attacked ; but although chiefly restricted to comparatively simple cases,\* and apparently yielding numbers which are doubly, if not trebly, specific, that is, numbers which are dependent not only on the specific nature of the substances the reactivity of which is being measured, but also on that of the reagent employed, and even on that of the solvent, the method has already, in the hands of Menshutkin, Goldschmidt, Lobry de Bruyn, Hecht, Conrad and Brückner, Carrara, and others, yielded results of the highest interest.

It is natural that in the attempt to construct such a theory of reactivity, the alkyl haloids, in particular the iodides, should have received especial attention. These substances, besides being in general extremely reactive and of great practical importance, from their employment in many synthetical reactions of wide applicability, exhibit two peculiarities ; they are of a dualistic type, and many of their reactions bear a strong resemblance, although possibly only one of type and not of mechanism, to those which are characteristic of salts. Here, then, if anywhere, some insight into the hidden causes of reactivity among organic substances might legitimately be expected.

J. Wislicenus appears to have been the first investigator to attempt a determination of the reactivity of the alkyl haloids by means of velocity measurements (*Annalen*, 1882, 212, 239). He ascertained the time required by various alkyl haloids to react completely with ethyl sodioacetoacetate in ethyl-alcoholic solution. Although the experiments were not carried out at a strictly constant temperature, the results he obtained are of great interest and are very probably sufficiently accurate for comparative purposes. In the following table, the numbers given are inversely proportional to the times required for complete reaction, these numbers being probably proportional to the specific velocity-coefficients, for, from the equation

$$-dc/dt = k\phi(c),$$

one obtains

$$dt = -\frac{1}{k} \frac{dc}{\phi(c)},$$

\* By "simple" cases are meant those reactions the progress of which is uniquely determined by a single specific velocity-coefficient—a very limited class in organic chemistry.

and therefore

$$t \text{ (time of reaction)} = \frac{1}{k} \int_0^{c_0} \frac{dc}{\phi(c)},$$

where  $c_0$  = initial equivalent concentration (which was always the same).

*Wislicenus's Experiments.*

Iodide.	Relative velocity.	Iodide.	Relative velocity.
Methyl .....	196	<i>iso</i> Propyl ...	1—9
Ethyl .....	21	<i>tert.</i> -Butyl ...	Excessively small
<i>n</i> -Propyl .....	5	Allyl .....	>784

These figures show at a glance the great reactivity of methyl iodide as compared with other saturated iodides and the enormous reactivity due to the presence of the unsaturated allyl group. Other experiments made by Wislicenus demonstrated, however, the extremely small reactivity of vinyl iodide, so that the mere presence of a double linking is not in itself sufficient to produce great reactivity.

How far now are such relative "reactivity-coefficients" independent of the particular reagent (ethyl sodioacetoacetate) employed, that is, how far do they possess what may be called a singly specific character? This very interesting question may be answered by considering the results of other kinetic investigations dealing with the alkyl haloids.

In 1890, Menshutkin (*Zeit. physikal. Chem.*, 1890, 5, 589) investigated the velocity of combination with triethylamine in acetone solution at 100°. The reaction was found to be bimolecular, and the relative values of the velocity-coefficients found by him are given in the following table.

*Menschutkin's Experiments.*

Iodide.	Relative velocity-coefficient.	Iodide.	Relative velocity-coefficient.
Methyl .....	1140	<i>n</i> -Butyl .....	1·38
Ethyl .....	10·1	<i>n</i> -Heptyl .....	1·08
<i>n</i> -Propyl .....	1·93	<i>n</i> -Octyl.....	1

So far as the comparison extends, a striking resemblance between these results and those obtained by Wislicenus is at once evident. For example, methyl iodide is seen to be pre-eminently reactive in both series. Again, ethyl iodide is four times as reactive as *n*-propyl iodide in Wislicenus's reaction, and about five times as reactive in Menshut-

kin's reaction. Broadly speaking, therefore, these relative velocity-coefficients would appear to possess the character of reactivity-coefficients. We cannot, however, expect *a priori* to obtain identical series of reactivity-coefficients except by comparing velocity-coefficients at the same temperature and in the same solvent, for we know that this is not possible even in the case of substances possessing dualistic or salt-like character. That this is actually true in the case of the alkyl iodides is shown by considering the results obtained by Hecht, Conrad, and Brückner (*Zeit. physikal. Chem.*, 1889, 4, 273) in their study of the formation of ethers from the alkyl iodides and sodium ethoxide in ethyl-alcoholic solution at 30°.\* This reaction was also found to obey a bimolecular velocity-equation. The relative velocity-coefficients are tabulated below.

*Experiments of Hecht, Conrad, and Brückner.*

Relative velocity-coefficient.		Relative velocity-coefficient.	
Iodide.		Iodide.	
Methyl .....	61.72	isoPropyl .....	0.92
Ethyl .....	4.87	n-Heptyl .....	1.04
n-Propyl .....	1.71	n-Octyl.....	1.00

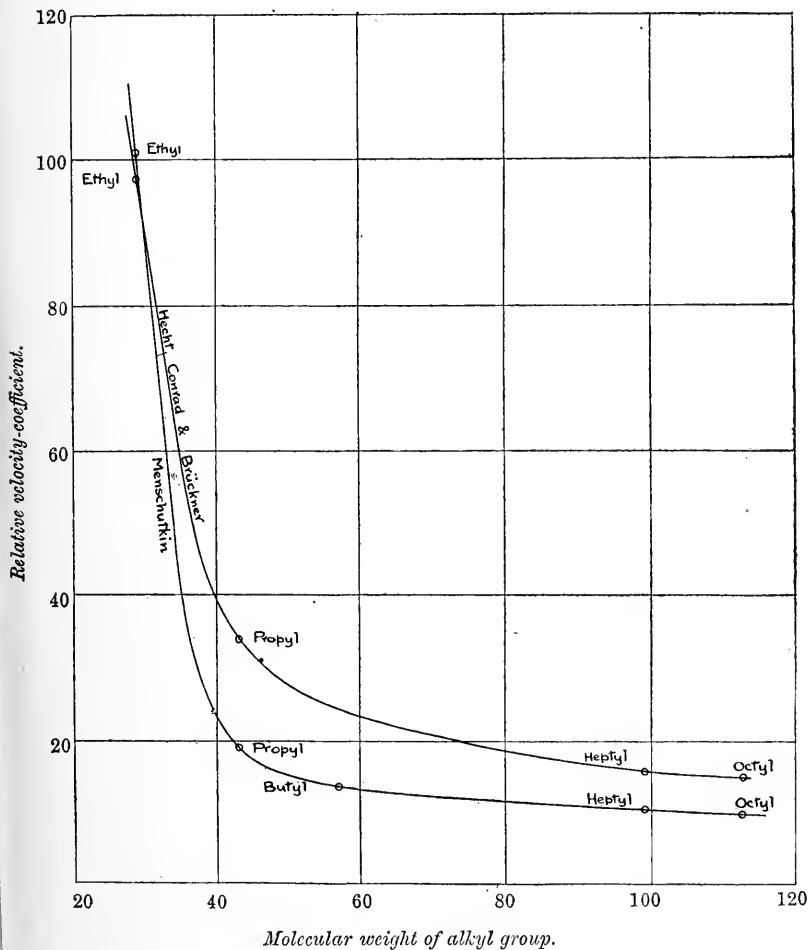
These figures exhibit a remarkable qualitative resemblance to those previously discussed, and in the cases of *n*-octyl, *n*-heptyl, and *n*-propyl iodides, even an approximately quantitative agreement with Menschutkin's figures; nevertheless, in the cases of ethyl and methyl iodides the quantitative comparison breaks down—as, indeed, might fairly be expected for the reasons given above. One important conclusion can, however, be drawn from all these results, namely, that in the reactions studied by Wislicenus, Menschutkin and Hecht, Conrad and Brückner, the reactivity of the alkyl iodides is due to the same condition or function of the molecule. This is rendered very evident by an inspection of Fig. 1 (p. 559), in which the general resemblance between the two curves is very striking.

The complexity of the problem of reactivity even in the relatively simple cases of the iodides becomes, however, at once apparent when we consider another type of reaction. The alkyl iodides, when heated with alcoholic potash or soda, yield in general a mixture of olefine and ether. This reaction has been studied very carefully and exhaustively by Nef (*Annalen*, 1899, 309, 126), but not with the object of determining relative velocity-coefficients. However, S. Brussoff (*Zeit. physikal. Chem.*, 1900, 34, 129) carried out a series of experiments dealing with this point. The alkyl iodides were heated

\* Somewhat similar experiments on a less extensive scale were made by F. Lengfeld (*Amer. Chem. J.*, 1889, 11, 40).

at 78°, with an approximately 2*N* solution of caustic potash in 96 per cent. alcohol. In Brussoff's experiments, the reaction mixture was not initially at 78°, so that the velocity of the reaction, measured by the

FIG. 1.



rate of evolution of the gaseous olefine, increased to a maximum and then fell regularly. In the following table are given the relative maximum velocities determined in this manner.

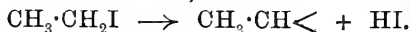
*Brussoff's Experiments.*

Iodide.	Relative maximum velocities of the evolution of olefine.	Iodide.	Relative maximum velocities of the evolution of olefine.
Ethyl.....	1.66	isoButyl.....	2.84
Propyl .....	2.24	sec.-Butyl .....	5.06
isoPropyl .....	2.84	tert.-Butyl .....	8.00
n-Butyl.....	1.00		

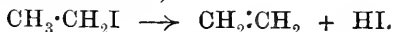
These figures are not nearly so trustworthy for the purposes of comparing the reactivity of the iodides as those quoted previously, since they only yield a measure, and that at best a rough one, of the rate of one of two reactions which are simultaneously brought about by the action of the alcoholic potash. A determination under conditions of constant temperature of the rate of diminution of alkalinity in the solution would probably have yielded numbers of much greater comparative value (compare Lobry de Bruyn and Steger, *Rec. trav. chim.*, 1899, 18, 41, 311). In spite of this, however, it is clear that we have here to deal with some molecular function or condition differing essentially from that observed in the cases cited previously. Thus *tert.*-butyl iodide is characterised by maximum reactivity, whereas in Wislicenus's experiments exactly the opposite is the case. Again, *isopropyl* iodide is more reactive than *n*-propyl iodide, and both more so than ethyl iodide. This is in direct opposition to the reactivities measured by Hecht, Conrad, and Brückner. It is clear that in the case of aqueous alcoholic potash the inner mechanism whereby the alkyl iodides react is quite different from that involved in the reactions with ethyl sodio-acetoacetate, triethylamine, and sodium ethoxide (in absolute alcohol). Hence, in the present state of our knowledge, any attempt to establish a general table of reactivities must meet with failure.

In the case of the reaction between the alkyl haloids and alcoholic potash, a theory of the mechanism of the process has been formulated by Nef (*loc. cit.*). He supposes that in alcoholic solution an alkyl haloid can undergo two modes of "dissociation," thus:

(a) "*Alkylidene*" dissociation,



(b) "*Alkylene*" dissociation,



The hydrogen iodide is neutralised by the caustic alkali or alkaline alkyloxide present, the free olefine is (in general) evolved as such, whilst the group  $\text{CH}_3\cdot\text{CH}$ : combines with alcohol to form an ether,  $\text{CH}_3\cdot\text{CH}< + \text{C}_2\text{H}_5\cdot\text{OH} = \text{C}_2\text{H}_5\cdot\text{O}\cdot\text{C}_2\text{H}_5$ . In proportion as the

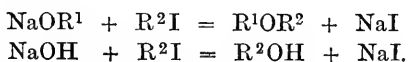
alkylene or alkylidene dissociation predominates, so, according to Nef, will the yield of olefine exceed that of ether or *vice versa*.<sup>\*</sup> In this connection, the following table of results given by Brussoff (*loc. cit.*) is important. The total possible yield of olefine was 300 c.c. in every case. The figures give in c.c. the volumes of olefine actually obtained under similar conditions of temperature and (equivalent molecular) concentration.

*Comparative Yields of Olefine (Brussoff).*

Iodide.	Volume of olefine (0°, 760 mm.).	Iodide.	Volume of olefine (0°, 760 mm.).
Ethyl.....	54	<i>iso</i> Butyl.....	265
<i>n</i> -Propyl .....	122	<i>sec.</i> -Butyl .....	290
<i>iso</i> Propyl .....	278	<i>tert.</i> -Butyl .....	245
<i>n</i> -Butyl .....	117		

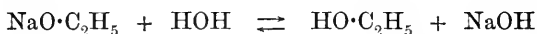
According to Nef's view, we must conclude from these figures that *isopropyl* and *isobutyl* iodides exhibit practically equal amounts of "alkylene" dissociation. It will be seen in what follows, however, that the velocity of reaction (in 100 per cent. alcohol) between *isopropyl* iodide and silver nitrate is at least one hundred and forty times greater than the velocity of reaction between *isobutyl* iodide and the silver salt. The result cannot be ascribed to the difference between the 96 per cent. alcohol employed by Brussoff and the absolute alcohol used in the experiments described below (compare p. 586), nor can it be explained on Nef's view by assuming that we have to deal with "alkylidene" dissociation in the reaction with silver nitrate, since, according to this investigation, the silver nitrate is converted into silver iodide by the reaction  $\text{AgNO}_3 + \text{HI} = \text{AgI} + \text{HNO}_3$ , and, for this purpose, hydrogen iodide produced by either sort of dissociation would appear to be equally efficient. There does not appear, therefore, to be any "dissociation" independent of the particular reagent employed, in which case alone can the concept of dissociation lead to results capable of experimental verification.

The formation of alcohol and ether can apparently be explained by Nef's assumption of "alkylidene" dissociation, but, as the actual existence of such a substance as, say,  $\text{CH}_3\text{:CH<}$  (ethylidene) is as yet problematical, it would seem much more natural to ascribe the formation of alcohol and ether (as is usually done) to the simultaneous reactions :



<sup>\*</sup> The problem is, however, complicated by the relative velocities of the processes of alkylene and alkylidene dissociations which are assumed to occur (see p. 563).

This involves, however, the assumption that sodium ethoxide, for example, can exist to some extent in an aqueous solution of alcohol. There are, however, very good reasons for believing that the equilibrium



really exists. Thus it is known that very dry alcohol cannot be completely dehydrated by distillation from sodium. The chief evidence is, however, afforded by the important researches of Lobry de Bruyn and A. Steger (*Rec. trav. chim.*, 1897, 18, 41 and 311).

The above equation represents in fact the hydrolysis of the salt,  $\text{Na}\cdot\text{OC}_2\text{H}_5$ , of "oxethylic" acid,  $\text{H}\cdot\text{OC}_2\text{H}_5$ , that is to say, the distribution of a base between the two acids  $\text{H}(\text{OH})$  and  $\text{H}(\text{OC}_2\text{H}_5)$ . Probably there is not a very great difference between the dissociation-constants of these two acids.

There is another point which must be carefully kept in mind in this connection. In order to explain the formation of a considerable amount of ether, it is not necessary to assume the pre-existence in the solution of a considerable amount of ethoxide. The actual output of ether (as compared with that of alcohol) depends also on the relative velocity of the reaction in which it is produced. Tautomeric equilibria and the outputs of reactions in which a reagent acts on one of the "dynamic" isomerides with relatively great velocity, have drawn attention in recent years to this important kinetic argument (Schiff, *Ber.*, 1898, 31, 205).

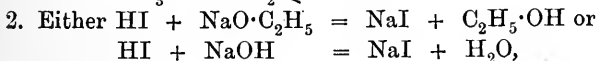
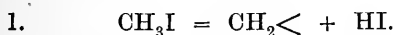
Considerable light is thrown on the question of alkylidene dissociation by the kinetic investigations of Lobry de Bruyn and Steger (*loc. cit.*). Consider the case of methyl iodide, where no alkylene dissociation is possible. The following table gives the mean values of the bimolecular velocity-coefficients for the reaction between methyl iodide and a solution of sodium in various mixtures of alcohol and water. The concentrations of the reacting substances were approximately  $N/20$ .

Percentage of Ethyl alcohol.	Mean velocity-coefficient.	Percentage of Ethyl alcohol.	Mean velocity-coefficient.
100	0.189	40	0.034
90	0.155	30	0.023
80	0.120	20	0.011
70	0.087	10	0.0062
60	0.066	0	0.0042
50	0.046		

In terms of Nef's theory, one may now assume either that (a) alkylidene dissociation is much greater in alcohol than in water, or that (b) the velocity of alkylidene dissociation is greater in alcohol than

in water; in the latter case, it is assumed that the neutralisation of the hydrogen iodide by sodium ethoxide or hydroxide proceeds very much faster than the dissociation of the alkyl iodide.

With respect to these assumptions, (a) is extremely improbable, considering the higher dissociating action of water, and (b) is purely gratuitous. The question of the order of the reaction may be now considered. According to Nef's theory, the reaction is the resultant of two others:



or the concurrent operation of these changes.

There are now several possibilities:—

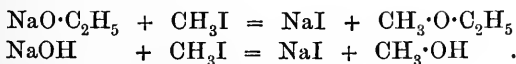
(a) The reaction or reactions enumerated under 2 proceed with relatively great velocity. We then measure the velocity of the unimolecular reaction indicated by 1.

(b) Reaction 1 proceeds with relatively great velocity. Even in the case of the aqueous solution where reaction 2 certainly possesses an enormously great velocity-coefficient, this assumption is a possible one, for if the alkylidene dissociation be of a sufficiently small order, the reaction 2 will proceed with measurable velocity. We now measure—to take the case of the aqueous solution—the velocity of the reaction  $\text{NaOH} + \text{HI} = \text{NaI} + \text{H}_2\text{O}$ . We may put  $c_{\text{OH}} = c_{\text{NaOH}}$ , and we must always have  $c_{\text{HI}} \times c_{\text{CH}_2} = k c_{\text{CH}_3\text{I}}$ , or since  $c_{\text{HI}} = c_{\text{CH}_3}$ ,  $c^2_{\text{HI}} = k c_{\text{CH}_3\text{I}}$ .

Hence, if  $v$  denote the velocity of the reaction,  $v = k' c_{\text{NaOH}} \sqrt{c_{\text{CH}_3\text{I}}}$ . (We may safely put  $c_{\text{H}} = c_{\text{HI}}$ ). So that in this case also the reaction will not proceed according to a bimolecular equation.

(c) The velocities of reactions 1 and 2 may be of the same order of magnitude. In this case the state of affairs will be very complicated, but it is very improbable that the bimolecular reaction-equation would be obeyed.

The evidence afforded by the results of Lobry de Bruyn and Steger would appear, therefore, to be against Nef's theory of alkylidene dissociation. It would seem much more reasonable to assume, as they do, the existence of the simultaneous reactions,



The velocity would then be expressed by the equation

$$v = k c_{\text{NaOEt}} \cdot c_{\text{CMeI}} + k' c_{\text{NaOH}} \cdot c_{\text{CMeI}}.$$

Let  $c_{\text{NaOEt}} / (c_{\text{NaOEt}} + c_{\text{NaOH}}) = \lambda$ ; then  $c_{\text{NaOH}} / (c_{\text{NaOEt}} + c_{\text{NaOH}}) = 1 - \lambda$ , and if we put

$$c_{\text{NaOH}} + c_{\text{NaOEt}} = c_{\text{Na}}$$

we obtain

$$v = k\lambda c_{\text{Na}} \cdot c_{\text{CH}_3\text{I}} + k'(1 - \lambda)c_{\text{Na}} \cdot c_{\text{CH}_3\text{I}}$$

or

$$v = \{k' + \lambda(k - k')\}c_{\text{Na}} \cdot c_{\text{CH}_3\text{I}}.$$

This is the equation of a bimolecular reaction, provided  $\lambda$  does not vary with  $c_{\text{Na}}$  during the course of the change.

This will be so provided that the adjusting equilibrium



proceeds with sufficient rapidity, for from this equation it follows that

$$\lambda / (1 - \lambda) = K \frac{c_{\text{EtOH}}}{c_{\text{H}_2\text{O}}}.$$

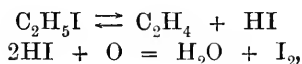
The ratio  $c_{\text{EtOH}} / c_{\text{H}_2\text{O}}$  will, however, remain practically constant during the reaction.

It is possible, therefore, to explain the results obtained by Lobry de Bruyn and Steger in the manner indicated, whereas it is difficult to see how they can be interpreted by the assumption of alkylidene dissociation.

When the alkylene dissociation assumed by Nef is considered, the matter is somewhat different. Both the products of the assumed dissociation are known substances. Moreover, it is difficult otherwise to understand the mechanism whereby olefine is produced, unless we relinquish any attempt to explain this mechanism by the formation of substances which pre-exist in the solution independently of the reagent and simply assume a "tendency" on the part of the alkyl iodide molecule to decompose in a certain way. The assumption of such a tendency, without the presence in the solution of the resulting products, is one which, in the present state of knowledge, eludes all precise treatment.

It is a fact in favour of Nef's assumption of alkylene dissociation that such a change has been actually shown to occur in the case of the heated vapours of alkyl bromides. Thus, for example, Aronstein (*Rec. trav. chim.*, 1880, 1, 134), who has investigated the dissociation of *n*-propyl and *isopropyl* bromides by Victor Meyer's air-displacement method, finds that at 210° these alkyl haloids are dissociated to the extent of 10.4 and 21.1 per cent. respectively. Similarly, Roozeboom (*Ber.*, 1881, 14, 2396) found that at 204° 60 per cent. of *tert.*-butyl

bromide undergoes dissociation. Hence a certain amount of the products of alkylene dissociation must exist in these vapours at every temperature, and therefore also in the liquids. It is possible also that the gradual discoloration of the alkyl iodides may be due to the following reactions :



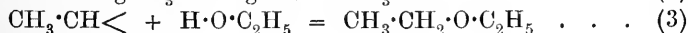
the latter action being accelerated by light.\*

The chief argument advanced by Nef in support of his theory is the behaviour of the alkyl iodides towards silver nitrate in alcoholic solution. If we employ no solvent or only dry ether, the reaction proceeds normally, according to the usual method for the preparation of esters. If, however, ethyl alcohol is present, free nitric acid, an ether, and in some cases an olefine† are formed, besides silver iodide and the corresponding alkyl nitrate.

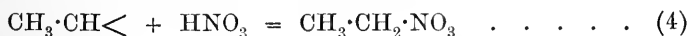
Thus methyl iodide gives free nitric acid and methyl ethyl ether; ethyl iodide yields nitric acid, diethyl ether, some ethyl nitrate, and a trace of ethylene. These reactions can be explained on Nef's theory by an alkylidene dissociation.



combined with the reactions



Any alkyl nitrate formed must then be due to the reaction :



Similarly, with propyl and *isopropyl* iodides in ethyl-alcoholic solution, the corresponding ethyl propyl ether and free nitric acid are produced. In the case of *isopropyl* iodide, however, a considerable amount of propylene is formed, which on Nef's theory points to an alkylene dissociation of this substance; this may be compared with the greater alkylene dissociation in the state of vapour of *isopropyl* bromide as compared with *n*-propyl bromide.

In the case of *isobutyl* iodide, it is necessary to assume both alkylene and alkylidene dissociations in order to explain the products of the reaction, which in one experiment were as follows :

\* The bromides, however, exhibit a similar change and in this case an analogous explanation is scarcely admissible.

† In the reaction between silver nitrate and ethyl iodide in aqueous solution, ethyl alcohol and nitric acid are formed besides silver iodide and ethyl nitrate.

	Per cent. of calculated amount.
Free nitric acid.....	46
Ethyl <i>tert.</i> -butyl ether .....	21
Ethyl <i>isobutyl</i> ether.....	5
<i>iso</i> Butyl nitrate.....	16
<i>iso</i> Butylene .....	29

It may be remarked that, from *isobutyl* iodide and alcoholic potash, Nef obtained 99 per cent. of the calculated amount of *isobutylene*, but no ethyl *isobutyl* ether; that is, in the presence of caustic potash there is only alkylene dissociation, whereas in the presence of silver nitrate both types of dissociation occur. But as the function of the caustic potash or silver nitrate according to the above view of the reaction is simply to remove the hydrogen iodide as fast as it is formed, it is difficult to see how the manner of dissociation of the alkyl iodide can be thereby affected.

In spite of this difficulty, it may be said that Nef's theory is the only rational attempt as yet put forward to explain the reaction between the alkyl iodides and silver nitrate in alcoholic solution. Although this reaction appears to be a very complicated one, its careful study from a kinetic standpoint might be expected to throw light on the causes which give rise to the reactivity of the alkyl haloids, and in particular to furnish evidence bearing on the validity of Nef's theory. In 1895, Chiminello (*Gazzetta*, 1895, 25, [ii], 410) described a few experiments which show that in equivalent *N*/20 solutions of ethyl iodide and silver nitrate in alcohol at 0°, the velocity of the reaction obeys the equation  $-dc/dt = kc^2$ . This would seem to point to a bimolecular reaction, which might be explained by assuming that the primary reaction is  $C_2H_5I + AgNO_3 = AgI + C_2H_5 \cdot NO_3$ . On raising the temperature to 10° or 15°, Chiminello found that the above equation was no longer obeyed, the value of the coefficient *k* falling off considerably as the reaction progressed. This he attributes to secondary reactions whereby the alcohol is oxidised to acetic acid\* and aldehyde. With methyl alcohol as solvent, he failed to obtain a constant coefficient in the foregoing velocity-equation, even at 0°.

On the basis of these and some other results, Nef's theory has been unfavourably criticised by E. von Biron (*J. Russ. Phys. Chem. Soc.*, 1900, 30, 667).

Taking the case of ethyl iodide and silver nitrate, we must have, according to Nef, a primary alkylidene dissociation (1) together with three other subsequent reactions (see p. 565). Measuring the velocity by the rate of disappearance of silver nitrate from the solution, we have to deal with reactions (1) and (2). Since (2) is an ionic reaction, it will pro-

\* As will be shown later, no acetic acid is formed under these conditions.

ceed with an incomparably greater speed than (1), hence the velocity measured will be that of reaction (1). But this is a unimolecular reaction; that is, it will obey the equation  $-dc/dt = kc$ , which is not in agreement with Chiminello's results at  $0^\circ$ .

This reasoning may be expressed as follows :

For reaction (1), we have

$$-dc_{\text{EtI}}/dt = k_1 c_{\text{EtI}} \quad . \quad . \quad . \quad . \quad . \quad (a).$$

For reaction (2)

$$-dc_{\text{AgNO}_3}/dt = k_2 c_{\text{AgNO}_3} \cdot c_{\text{HI}} \quad . \quad . \quad . \quad (b).$$

If (2) proceeds very much faster than (1), the value of  $c_{\text{HI}}$  will be extremely small, so that the value of  $c_{\text{EtI}}$  is sensibly equal to that of  $c_{\text{AgNO}_3}$  at every moment. Putting  $c_{\text{EtI}} = c_{\text{AgNO}_3} = c$ , we obtain the equations :

$$-dc/dt = k_1 c \quad . \quad . \quad . \quad . \quad . \quad (c),$$

$$-dc/dt = k_2 c \cdot c_{\text{HI}} \quad . \quad . \quad . \quad . \quad . \quad (d),$$

whence  $c_{\text{HI}}$  possesses the small constant value  $k_1/k_2$ , and equation (d), which is the one we really measure, assumes the same form as (c), that is, the unimolecular form. This argument is, however, inconclusive, because, even although we grant that  $k_2$  is, say, ten thousand times greater than  $k_1$ , the value of  $c_{\text{HI}}$  corresponding with the dissociation-equilibrium,  $\text{C}_2\text{H}_5\text{I} \rightleftharpoons \text{C}_2\text{H}_4 + \text{HI}$ , may very well be extremely small, say ten thousand times smaller than  $c_{\text{EtI}}$ , in which case the velocity of establishment of the above equilibrium may be of the same order of magnitude as the velocity of reaction (2).

A further discussion of this point must be deferred until we come to consider the bearing of the experimental results obtained in the present paper.

The other objections advanced by E. von Biron have no weight, as they are evidently due to a misunderstanding. He forgets that in Nef's theory both alkylene and alkylidene dissociations are supposed to occur, and so considers, as arguments against the theory, the fact that *tert.*-butyl iodide reacts with silver nitrate and that ethyl *iso*-propyl ether is obtained from *isopropyl* iodide, whereas ethyl *n*-propyl ether results from *n*-propyl iodide.

### *Experimental Results.*

The experiments described in this paper were carried out with the object of examining in detail the velocity of reaction between the alkyl iodides and silver nitrate in alcoholic solution.

The ethyl alcohol employed was carefully dehydrated by repeated boiling for many hours with fresh calcium oxide, the reflux condenser

being fitted with a calcium chloride guard-tube. After fractionation from the calcium oxide, it was found necessary to boil the alcohol gently for an hour or two with some silver nitrate, from which it was then finally distilled. Solutions of silver nitrate in alcohol purified in this manner could be kept in the dark for weeks without exhibiting any perceptible formation of silver. If the above precaution was not taken, the alcoholic silver nitrate solutions rapidly assumed a violet colour owing to the reduction of a small quantity of the silver nitrate by some impurity (aldehyde?) contained in the alcohol.

The alkyl iodides were shaken with silver powder, dried over calcium chloride, and fractionated.

Alcoholic solutions of silver nitrate and of the various iodides were prepared of such a strength that when equal volumes of each were mixed the resultant solution would have the required composition. In every case, a total volume of 6 c.c. was employed, 3 c.c. of alcoholic silver nitrate or alkyl iodide solution being separately warmed in the thermostat and then mixed in a small Erlenmeyer flask. In this way, various flasks were prepared and heated for different lengths of time in the thermostat. The flasks were kept tightly corked, and were covered with black cloth to exclude light. To stop the reaction in any flask at a given moment, a measured volume of  $N/100$  ammonium thiocyanate solution was quickly run in, the amount added being always in slight excess of that required to precipitate the whole of the silver remaining in solution. By subsequent titration of this excess of thiocyanate with  $N/100$  silver nitrate, using a ferric indicator, the amount of silver nitrate in the solution at the moment when the reaction was stopped could be readily determined.

The unit of mass employed in the following tables is the amount of silver nitrate contained in 1 c.c. of a  $N/100$  silver nitrate solution. Thus, as 6 c.c. of a  $N/40$  silver nitrate solution contain as much of the salt as 15 c.c. of a  $N/100$  solution, the mass of silver nitrate contained therein is 15. The unit of volume employed is 6 c.c. Hence the concentration of a  $N/40$  silver solution is 15, since it contains 15 of these units of mass per unit volume. It is clear, therefore, that in this system of units the concentration of the solution at any moment is equal to the number of c.c. of  $N/100$  thiocyanate required to precipitate exactly all the contained silver nitrate (since the total volume of the solution was always 6 c.c.).

The concentration of the alkyl iodide is expressed in terms of equivalent units, that is, the unit of mass of any alkyl iodide is the amount which is chemically equivalent to the silver nitrate contained in 1 c.c. of a  $N/100$  silver nitrate solution, chemical equivalence being defined for this purpose by the relation  $RI \equiv AgNO_3$ , where the symbol  $\equiv$  denotes chemical equality or equivalence.

All the experiments described in this paper were carried out at a constant temperature of  $24.5^{\circ}$  (except where otherwise stated). The values of  $k$  given in the following tables were calculated in the case of equivalent solutions by means of the bimolecular velocity equation,  $-dc/dt = kc^2$ , so that  $k = 1/t(1/c - 1/c_0)$ , where  $c_0$  = concentration at the time-zero,  $c$  = concentration at time  $t$  (unit of time = one minute). The time-zero was sometimes the moment of mixing the solutions, sometimes a time-point approximately ten minutes later.

Table 1.  $N/40$   $\text{CH}_3\text{I}$ ;  $N/40$   $\text{AgNO}_3$ ; solvent, ethyl alcohol.

Time.	Concentration of $\text{AgNO}_3$ .	Value of $k$ .
0	12.90	—
16.24	10.75	0.00095
35.49	9.05	0.00092
62.22	7.35	0.00094
100.62	5.70	0.00097
129.97	5.05	0.00092
179.80	4.10	0.00092

Table 2.  $N/40$   $\text{C}_2\text{H}_5\text{I}$ ;  $N/40$   $\text{AgNO}_3$ ; solvent, ethyl alcohol.

Time.	Concentration of $\text{AgNO}_3$ .	Value of $k$ .
0	15.00	—
10.37	11.00	0.00233
20.03	9.35	0.00201
38.19	6.78	0.00211
51.67	5.45	0.00226
74.50	4.50	0.00208
105.35	3.42	0.00214
143.18	2.70	0.00212
194.00	1.98	0.00223

Table 3.  $N/40$   $n$ -propyl iodide;  $N/40$   $\text{AgNO}_3$ ; solvent, ethyl alcohol.

Time.	Concentration of $\text{AgNO}_3$ .	Value of $k$ .
0	15.00	—
10.12	12.95	0.001042
27.71	10.70	0.000966
47.20	8.90	0.000968
74.11	7.30	0.000948
106.86	6.00	0.000935
152.52	4.50	0.001018
198.52	3.75	0.001007

Table 4.  $N/40$   $n$ -butyl iodide;  $N/40$   $\text{AgNO}_3$ ; solvent, ethyl alcohol.

Time.	Concentration of $\text{AgNO}_3$ .	Value of $k$ .
0	13.35	—
15.82	11.60	0.000714
32.41	10.20	0.000713
57.06	8.80	0.000678
97.48	7.05	0.000686
119.50	6.45	0.000670
145.47	5.73	0.000684
192.31	4.95	0.000660

Table 5. *N*/40 isobutyl iodide; *N*/40 AgNO<sub>3</sub>; solvent, ethyl alcohol.

Time.	Concentration of AgNO <sub>3</sub> .	Value of <i>k</i> .
0	14.80	—
34.34	13.75	0.000150
77.00	12.70	0.000145
108.83	12.10	0.000138
196.75	10.60	0.000136
213.55	10.35	0.000136
244.91	10.00	0.000132
280.25	9.65	0.000128

Table 6. *N*/40 isoamyl iodide;\* *N*/40 AgNO<sub>3</sub>; solvent, ethyl alcohol.

Time.	Concentration of AgNO <sub>3</sub> .	Value of <i>k</i> .
0	13.50	—
22.07	11.50	0.000583
42.84	10.50	0.000593
79.25	8.30	0.000585
110.07	7.45	0.000546
145.66	6.60	0.000531
212.64	5.20	0.000555

The attempt to obtain the value of *k* for isopropyl iodide under similar conditions proved unsuccessful, owing to the relatively enormous velocity of this reaction. Thus, in *N*/40 solutions at 24.5° only about 2 per cent. of the original amount of silver nitrate remained in solution after 10 minutes. An experiment made with *N*/200 solutions of both isopropyl iodide and silver nitrate at the temperature of the laboratory (17°), which probably did not vary appreciably during the hour required for the determination, gave the following results:

Table 7. *N*/200 isopropyl iodide; *N*/200 AgNO<sub>3</sub>; solvent, ethyl alcohol.

Time.	Concentration of AgNO <sub>3</sub> .	Value of <i>k</i> .
0	3.00	—
6.83	2.12	0.0202
10.00	1.90	0.0192
15.00	1.55	0.0207
20.42	1.30	0.0213
38.42	0.75	0.0260

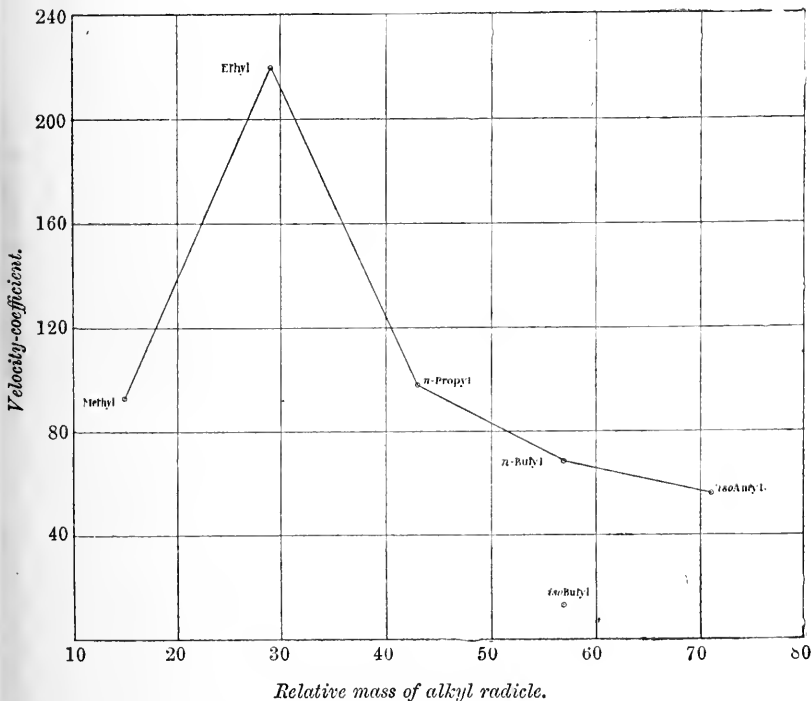
These experiments, which provide us with a series of exact numbers † (velocity-coefficients) representing the reactivities of the alkyl iodides in alcoholic solution, as measured by the reacting silver nitrate, form, in some respects, a remarkably striking contrast to the experiments of Hecht, Conrad, and Brückner, in which the reactivities of the same substances dissolved in the same solvent were determined by a different reagent, namely, sodium ethoxide, but by exactly the same method.

\* This is the "isoamyl iodide" as sold by Kahlbaum.

† See Table 12 (p. 573).

Thus, in the experiments of these investigators, methyl iodide reacts thirteen times as rapidly as ethyl iodide and sixty-seven times as rapidly as *isopropyl* iodide, whereas in the foregoing experiments, ethyl iodide reacts two and a third times as rapidly as methyl iodide, and *isopropyl* iodide at least twenty-two\* times as rapidly. A greater contrast could not well be imagined, nor a better proof produced that no general tables of the reactivities of organic compounds of similar type can be constructed. The order of magnitude of the velocity-

FIG. 2.



coefficients obtained in the above experiments is very peculiar. Considering only the alkyl radicles of normal structure, the results shown graphically in Fig. 2 exhibit, in a striking manner, the anomalous position occupied in the "curve" by methyl iodide. If Nef's theory were established and it could be shown that the alkylene dissociation was the predominating one, or the one which occurred with the greatest velocity, the low value of the velocity-coefficient of

\* If *isopropyl* iodide had been measured in *N*/40 solution, this ratio would be much greater (compare p. 575).

methyl iodide might possibly be explained, since, in this case, an alkylidene dissociation only can occur. But the same difficulty occurs here as that referred to previously, namely, that this argument would apply equally well to the case where sodium ethoxide is the reagent, whereas in this instance methyl iodide is distinguished by a pre-eminently great velocity-coefficient.

Similarly, if we were to attempt to explain the great reactivity of isopropyl iodide in the present case by a relatively great alkylene dissociation or a relatively great velocity of alkylene dissociation, it is not clear why the reactivity of isopropyl iodide towards sodium ethoxide should be relatively so small.\*

Summarising the results obtained, we may say that whilst the reactivities of ethyl, *n*-propyl, *n*-butyl, and isoamyl iodides appear to stand in some sort of regular relation to the relative masses of the alkyl radicles, methyl and isobutyl iodides are characterised by an abnormally low, and isopropyl iodide by an abnormally high reactivity.

In all the preceding experiments, it was found that, after the necessary intervals of time, the whole of the silver was precipitated. In order to prove directly, however, that this precipitate consisted of silver iodide and did not contain any of the double compound of silver iodide and nitrate precipitated in Zeisel's method of estimating alkoxy groups, a weighed quantity of the precipitate obtained in the reaction between  $N/40$  silver nitrate and  $N/40$  ethyl iodide was digested with water and a few drops of nitric acid and then filtered and dried. Its weight was found to be unchanged.

Confirmatory evidence of the complete reaction between the silver and the iodine was obtained in an experiment carried out with propyl iodide, in which, after equivalent quantities of this compound and silver nitrate had been allowed to react, until the solution contained no soluble silver salt, a measured volume of silver nitrate solution of known strength was added, and the flask left for 24 hours in the thermostat. Subsequently, on titrating with thiocyanate, the whole of this silver was found to be present in the solution.

It should also be mentioned that in every case the reaction-mixture became strongly acid (Nef, *loc. cit.*). Reference to this point will be made later (see page 586).

In order to ascertain how far the velocity of the reaction depended on the particular alcohol employed as solvent, a parallel series of experiments was carried out with methyl alcohol. The results are given in the four following tables:

\* Compare also the enormous difference in reactivity between isopropyl and isobutyl iodides (as measured by the above experiments) with their practically equal reactivities towards alcoholic potash as measured by Brussoff (see p. 560). It is difficult to reconcile these results with Nef's theory.

Table 8.  $N/40$   $\text{CH}_3\text{I}$ ;  $N/40$   $\text{AgNO}_3$ ;  
solvent, methyl alcohol.

Time.	Concentration of $\text{AgNO}_3$ .	Value of $k$ .
0	15.00	—
10.75	11.60	0.00235
18.50	9.90	0.00185
36.75	7.50	0.00181
62.50	5.80	0.00173
90.92	4.60	0.00165
117.17	3.75	0.00170
166.25	2.90	0.00167
212.63	2.25	0.00177

Table 9.  $N/40$   $\text{C}_2\text{H}_5\text{I}$ ;  $N/40$   $\text{AgNO}_3$ ;  
solvent, methyl alcohol.

Time.	Concentration of $\text{AgNO}_3$ .	Value of $k$ .
0	15.00	—
5.03	11.00	0.00482
10.46	8.90	0.00436
15.95	7.18	0.00455
20.87	6.17	0.00457
25.12	5.63	0.00441
36.42	4.40	0.00441
51.36	3.60	0.00411
79.95	2.50	0.00416
110.78	1.80	0.00441

Table 10.  $N/40$   $n$ -propyl iodide;  
 $N/40$   $\text{AgNO}_3$ ; solvent, methyl  
alcohol.

Time.	Concentration of $\text{AgNO}_3$ .	Value of $k$ .
0	15.00	—
11.37	10.85	0.00224
19.33	8.85	0.00239
41.08	6.30	0.00223
61.08	4.95	0.00221
89.75	3.85	0.00214
121.17	2.85	0.00234
154.17	2.40	0.00227
192.08	2.00	0.00225

Table 11.  $N/40$   $n$ -butyl iodide;  
 $N/40$   $\text{AgNO}_3$ ; solvent, methyl  
alcohol.

Time.	Concentration of $\text{AgNO}_3$ .	Value of $k$ .
0	11.40	—
12.66	9.10	0.00175
31.07	7.20	0.00164
51.55	6.00	0.00153
81.88	4.75	0.00149
107.38	4.35	0.00132
146.21	3.40	0.00141

The mean values of the velocity-coefficients in both ethyl and methyl alcohols, together with their ratios, are given in the following table ( $N/40$  equivalent concentration; temperature  $24.5^\circ$ ):

Table 12. Mean values of velocity-coefficients.

Iodide.	$k_{\text{EtOH}}$ .	$k_{\text{MeOH}}$ .	$k_{\text{MeOH}}/k_{\text{EtOH}}$ .
Methyl	0.000935	0.00180	1.92
Ethyl	0.00220	0.00442	2.00
$n$ -Propyl	0.000984	0.00226	2.29
$n$ -Butyl	0.000686	0.00145	2.11
$iso$ Butyl	0.000138	—	—
$iso$ Amyl	0.000565	—	—

The constancy of the ratio  $k_{\text{MeOH}}/k_{\text{EtOH}}$  is noteworthy. As previously noticed by many other observers, the velocity is greater in the medium of higher dissociating power.

It is a well-known fact that the alkyl iodides, when exposed to light, slowly decompose, yielding free iodine which dissolves in the liquid, giving it a yellow or brown colour. With respect to the alcoholic solutions employed in the above experiments, it was observed that a relation appeared to exist between the reactivities as measured in the preceding experiments and the rate of this production of free iodine. Thus, in spite of many precautions, it was not possible to keep alcoholic solutions of *isopropyl* iodide for many days before the above decomposition became manifest, whilst an alcoholic solution of *isobutyl* iodide, which was prepared fifteen months ago and has been exposed to daylight continuously for more than six months, is still absolutely colourless.

In order to examine this interesting point further, a set of test-tubes was prepared containing  $N/20$  solutions of the different iodides in ethyl alcohol. These were securely corked and placed in a row on a table facing a window. On the following day, the solution of *isopropyl* iodide exhibited a faint coloration. The other solutions became coloured in due course in the relative order of their velocity-coefficients, as given in Table 12 or shown graphically on p. 571, with the exception of methyl iodide, which appeared to have a rate of decomposition intermediate between *isopropyl* and ethyl iodides. After six months of exposure to light, the colorations were as follows:

<i>iso</i> Propyl iodide	} Deep brown.	Butyl iodide	} Pale yellow.
Methyl iodide		<i>iso</i> Amyl iodide	
Ethyl iodide ...	} Bright yellow.	<i>iso</i> Butyl iodide	Colourless.
Propyl iodide...			

A comparison of this list with Fig. 2 shows at once that there is a remarkable parallelism between the two phenomena. That these effects are complex is shown, however, not only by the anomalous position of methyl iodide in the above list, but also by the fact that a solution of ethyl iodide in methyl alcohol appears to decompose even more rapidly than the solution of *isopropyl* iodide employed in the above experiments. As already stated (see p. 565), this formation of free iodine may possibly be due to an oxidation of hydrogen iodide, the latter resulting from the dissociation of the iodides. Further experiments on this point are, however, necessary.

So far as the measurements recorded in the foregoing tables go, the reaction between an alkyl iodide and silver nitrate in absolute alcoholic solution appears to be a simple bimolecular one. Were this in reality the case, the result would be of great importance in a discussion of

Nef's theory. As mentioned previously (see p. 566), the experiments of Chiminello have been utilised for this purpose by E. von Biron, although it was shown above that the conclusion arrived at by the latter is not valid, quite apart from the validity of his major premise, namely, that the reaction is, chemically speaking, a bimolecular one. Now, as is well known, in order to prove by kinetic investigations that a given non-reversible reaction is a truly bimolecular one in the chemical sense, it is necessary, not only to show that the velocity-coefficient is constant during the course of a particular reaction, but also that it does not vary with the initial concentration of the reacting mixture, provided that these concentrations are sufficiently small (less than about  $N/20$ ). In the experiments about to be described, the initial concentrations varied from  $N/20$  to  $N/80$ . The results obtained with butyl iodide are given in the following tables:

Table 13.  $N/20$  *n*-butyl iodide ;  
 $N/20$   $\text{AgNO}_3$  ; ethyl alcohol.

Time.	Concentration of $\text{AgNO}_3$ .	Value of $k$ .
0	24.15	—
4.32	21.80	0.00103
13.47	17.85	0.00108
24.95	14.90	0.00103
36.70	13.20	0.00117
54.03	11.05	0.00091
80.70	9.00	0.00086
125.11	7.20	0.00078

Table 14.  $N/50$  *n*-butyl iodide  
 $N/50$   $\text{AgNO}_3$  ; ethyl alcohol.

Time.	Concentration of $\text{AgNO}_3$ .	Value of $k$ .
0	10.70	—
18.68	9.53	0.000614
36.57	8.40	0.000699 (?)
57.59	7.70	0.000632
99.00	6.42	0.000629
138.75	5.55	0.000625
186.34	4.83	0.000609
233.23	4.17	0.000627

Table 15.  $N/80$  *n*-butyl iodide ;  
 $N/80$   $\text{AgNO}_3$  ; ethyl alcohol.

Time.	Concentration of $\text{AgNO}_3$ .	Value of $k$ .
0	6.95	—
40.74	6.10	0.000491
80.97	5.45	0.000489
143.75	4.75	0.000463
195.65	4.30	0.000453
277.32	3.70	0.000455

Table 16. *n*-Butyliodide; variation  
of mean velocity-coefficients  
with initial concentration.

Initial concentration of both $\text{C}_4\text{H}_9\text{I}$ and $\text{AgNO}_3$ .	Mean velocity- coefficients.
$N/20 = 0.0500$	0.00098
$N/40 = 0.0250$	0.00068
$N/50 = 0.0200$	0.00063
$N/80 = 0.0125$	0.00047

The values of  $k$  tabulated in Table 16 are the mean values obtained at different concentrations.

These numbers bring out at once the important fact that the velocity-coefficient of the bimolecular velocity-equation increases very

considerably with increase of initial concentration. The reaction is, therefore, not a simple bimolecular one, that is, its equation is not

$$dx/dt = k(A - x)^2,$$

but

$$dx/dt = k \cdot \phi(A) \cdot (A - x)^2,$$

where  $A$  = initial concentration and  $A - x$  = concentration at the time  $t$ . Hence, although from the chemical standpoint the reaction may still be bimolecular, this can only be proved, or at all events rendered probable, by explaining the variability of  $k$  with the initial concentration. It may be remarked in passing that the increase of  $k$  with increasing concentration does not favour the view that the mechanism of the reaction is connected with dissociation-phenomena.

In considering the law, according to which  $k$  varies with  $c$ , the logarithm of  $k$  was plotted against the logarithm of  $c$  on squared paper, and it was found that of the four points so obtained three lay exactly on a straight line, whilst the point corresponding to the  $N/50$  solution was considerably removed from this line. The obvious interpretation of this result is that some error has crept into this particular measurement, and that the phenomenon is represented by the exponential law,  $k = Kc^n$ . On calculating  $n$  by means of the equation

$$n = \frac{\log k_1 - \log k_2}{\log c_1 - \log c_2},$$

where correlated quantities are indicated by the same numerical suffix, we find the values 0.5272, 0.5299, and 0.5328, the mean of which is 0.53; hence  $k = Kc^{0.53}$ . We thus arrive at the result that the velocity-coefficient is approximately proportional to the square root of the initial (equivalent) concentration.

In order to obtain more data concerning the variation of the velocity-coefficient, and more particularly to ascertain how the variation in question is related to changes in the initial concentrations of each component, systematic experiments were now carried out with ethyl iodide. In the case of solutions not containing silver nitrate and iodide in equivalent concentrations, the value of  $k$  was calculated by means of the equation

$$-dc_1/dt = kc_1c_2.$$

Since the reacting substances disappear simultaneously in equivalent quantities,

$$dc_1 = dc_2, \text{ hence } c = c_1 + K.$$

Therefore

$$-\frac{dc_1}{c_1c_2} = -\frac{dc_1}{c_1(c_1 + K)} = \frac{1}{K} \left( \frac{dc_1}{c_1 + K} - \frac{dc_1}{c_1} \right) = \frac{1}{K} d \log \frac{c_1 + K}{c_1} =$$

$$\frac{1}{K} d \log \frac{c_2}{c_1} = d(kt),$$

whence

$$\frac{1}{K} \log \frac{c_2}{c_1} = kt + \text{const.}$$

Denoting initial concentrations by the suffix  $o$ ,  $\frac{1}{K} \log \frac{c_{02}}{c_{01}} = \text{const.}$ ,

hence

$$\frac{1}{K} \log \frac{c_2 c_{01}}{c_1 c_{02}} = \frac{1}{(c_{02} - c_{01})} \log \frac{c_2 c_{01}}{c_1 c_{02}} = kt. *$$

Table 17.  $N/40$   $C_2H_5I$ ;  $N/20$   $AgNO_3$ ; ethyl alcohol.

Time.	Concen- tration of $AgNO_3$ .	Value of $k$ .
0	30.00	—
4.58	24.60	0.00360
5.50	24.10	0.00340
9.75	21.30	0.00358
10.75	20.95	0.00350
14.67	19.45	0.00355
16.25	19.30	0.00329
26.00	17.50	0.00321
35.42	16.45	0.00326

Table 18.  $N/20$   $C_2H_5I$ ;  $N/40$   $AgNO_3$ ; ethyl alcohol.

Time.	Concen- tration of $AgNO_3$ .	Value of $k$ .
0	15.00	—
10.58	8.95	0.00183
20.83	5.60	0.00195
35.25	3.40	0.00188
49.75	2.20	0.00182
68.41	1.20	0.00185
88.33	0.70	0.00182

\* With ordinary logarithms

$$k = \frac{1}{0.4343(c_{02} - c_{01})t} \log \frac{c_2 c_{01}}{c_1 c_{02}}.$$

It is necessary to be careful about this point in comparing non-equivalent with equivalent reaction-mixtures, as in the latter case the formula is not logarithmic.

Table 19.  $N/40$   $C_2H_5I$ ;  $N/80$   $AgNO_3$ ; ethyl alcohol.

Time.	Concentration of $AgNO_3$ .	Value of $k$ .
0	7.50	—
11.34	5.90	0.00149
20.33	5.10	0.00138
35.33	3.90	0.00143
49.77	3.15	0.00140
68.58	2.45	0.00137
81.85	2.10	0.00134
133.92	1.15	0.00131
202.00	0.45	0.00143

Table 20.  $N/80$   $C_2H_5I$ ;  $N/40$   $AgNO_3$ ; ethyl alcohol.

Time.	Concentration of $AgNO_3$ .	Value of $k$ .
0	15.00	—
10.35	12.75	0.00250
20.03	11.70	0.00220
35.37	10.50	0.00210
51.45	9.30	0.00240
70.60	8.90	0.00218
101.61	8.10	0.00250

Table 21.  $N/80$   $C_2H_5I$ ;  $N/80$   $AgNO_3$ ; ethyl alcohol.

Time.	Concentration of $AgNO_3$ .	Value of $k$ .
0	7.50	—
12.11	6.50	0.00169
26.58	5.80	0.00147
45.42	4.95	0.00151
68.92	4.20	0.00152
108.27	3.45	0.00144
151.28	2.80	0.00147
210.67	2.30	0.00143
244.67	2.02	0.00147

Table 22. Mean velocity-coefficients for  $C_2H_5I$  and  $AgNO_3$  in ethyl alcohol.

Concentration of $C_2H_5I$ .	Concentration of $AgNO_3$ .	Value of $k$ .
$N/40$	$N/80$	0.00139
$N/80$	$N/80$	0.00150
$N/20$	$N/40$	0.00186
$N/40$	$N/40$	0.00220
$N/80$	$N/40$	0.00231
$N/40$	$N/20$	0.00342

The mean values of the velocity-coefficients are tabulated in table 22, and from this we learn the following facts:

1. In the case of solutions of equivalent initial concentrations, the value of  $k$  increases with increasing initial concentration as in the case of butyl iodide, and in the same ratio. Thus comparing  $N/80$  and  $N/40$  solutions, the ratio of the increase of  $k$  is 1.45 for butyl iodide and 1.46 for ethyl iodide.

2. When the initial concentration of the silver nitrate remains constant ( $N/40$ ) the value of  $k$  increases with diminishing concentration of ethyl iodide. Thus comparing  $N/20$  and  $N/80$  solutions, the ratio of increase is 1.24.

3. When the initial concentration of the ethyl iodide remains constant ( $N/40$ ), the value of  $k$  diminishes with diminishing initial

concentration of silver nitrate. The ratio of change is here very much greater; thus, comparing  $N/20$  and  $N/80$  solutions, the ratio of decrease is 2.46.

It is clear that the variation of  $k$  with the variation of the initial concentrations of the reacting components is chiefly due to the silver nitrate. For, whilst the values of  $k$  are in round numbers proportional to 19, 22, and 23 for constant initial concentration of silver nitrate, the corresponding values for constant initial concentration of ethyl iodide and varying initial concentration of silver nitrate are 14, 22, and 34.

This result throws some light on the inner mechanism of the reaction. For if the silver nitrate were supposed to react with practically infinite velocity on hydrogen iodide (or iodine ions) produced by a comparatively slow primary reaction (as in E. von Biron's interpretation of Nef's theory) then it would be very improbable that the concentration of the silver nitrate should exert such a profound influence on the intrinsic velocity of the whole reaction. It is, in fact, clear that the concentration and hence the molecular state of the silver nitrate in the alcoholic solution plays a very important part in determining the velocity. As regards the relation between the coefficient  $k$  and the initial concentration  $c$  of the silver nitrate (the initial concentration of the ethyl iodide remaining constant), it will be noticed that of the numbers 14, 22, and 34, the second is equal approximately to  $14 + \frac{1}{2} \times 14$  and the third is similarly equal to  $22 + \frac{1}{2} \times 22$ ; that is to say, these values of  $k$  are approximately in geometrical progression. Now the corresponding values of  $c$  are also in geometrical progression. But if two series of correlated numbers are each in geometrical progression, the functional relation between a correlated pair is of the form  $k = Kc^n$ . Applying this equation to calculate  $n$  in the manner indicated previously, the values 0.64 and 0.65 are obtained. The relation between  $k$  and  $c$  in this case approximates, therefore, to the equation  $k = Kc^{\frac{2}{3}}$ .

Hence in those cases where the initial concentration of the ethyl iodide remains constant, whilst that of the silver nitrate varies from  $N/20$  to  $N/80$ , it is found that the velocity of the reaction can be represented by the equation

$$-dc/dt = K\phi(c_{01})c_1^2c_2,$$

where  $c_1$  = concentration of  $\text{AgNO}_3$ ,  $c_2$  = concentration of  $\text{C}_2\text{H}_5\text{I}$ ,  $K$  = a constant, and  $c_{01}$  = initial value of  $c_1$  (as shown above,  $\phi(c_{01}) \equiv \frac{c_1^{\frac{2}{3}}}{c_{01}^{\frac{2}{3}}}$  approximately).

In any particular reaction the concentration of the silver nitrate continuously decreases, passing through the initial values of all reactions commencing with weaker solutions, and it is therefore clear

that the term  $\phi(c_{01})$  can only be regarded as a purely formal representation. In fact, the constancy of the velocity-coefficient in any particular reaction may be mathematically represented by expressing it as a function of  $c_{01}$ , but obviously its constancy cannot be explained by this means, that is to say, by representing it as a function of the initial value of a varying parameter, since so far as the manifold of values of this parameter is concerned, the initial value is of no more importance than any other. In considering whether any other mode of formulation is possible which might subsequently lend itself to chemical interpretation, this expression must satisfy two requirements.

(a) It must coincide mathematically with the foregoing, in order to represent the experimental data.

(b) It must express the velocity-coefficient of any particular reaction as a function of the concentration of some chemical parameter, which remains constant during the particular reaction; but which varies from one case to another if the initial concentration of the silver nitrate varies.

These conditions are both satisfied by writing  $\phi(c_{\text{NO}_3})$  instead of  $\phi(c_{01})$ , where  $c_{\text{NO}_3}$  is taken to be the concentration of the group  $\text{NO}_3$  in the reacting mixture, whether this occurs in  $\text{AgNO}_3$ ,  $\text{C}_2\text{H}_5\cdot\text{NO}_3$ ,  $\text{HNO}_3$ , or as free ion. Since, as will be shown presently, there is no appreciable oxidation of alcohol to acetic acid or aldehyde, the group  $\text{NO}_3$  is conserved in the reaction, and therefore satisfies the first part of condition (b). It is obvious that it satisfies the second part of (b), and as all concentrations are expressed in terms of equivalent units,  $c_{\text{NO}_3} = c_{01}$ , and thus condition (a) is also fulfilled.

The following differential equation,

$$-dc/dt = K\phi(c_{\text{NO}_3})c_1c_2,$$

therefore equally well expresses the results. This second formulation cannot, however, be regarded as standing in a much closer relation to the actual mechanism of the reaction, owing to the peculiar significance attached to  $c_{\text{NO}_3}$ . If no ethyl nitrate were formed, the  $\text{NO}_3$  of the  $\text{AgNO}_3$  all appearing as  $\text{HNO}_3$ , then by supposing the dissociation-constant of the  $\text{AgNO}_3$  to equal that of  $\text{HNO}_3$ , it would follow that  $c_{\text{NO}_3}$  (where this symbol now denotes the concentration of the  $\text{NO}_3$  ion) remains constant in any particular reaction. Since, moreover,  $c_{\text{NO}_3} = F(c_{01})$ , the differential equation might be written as

$$-c/dt = Kf(c_{\text{NO}_3})c_1c_2.$$

If the form of  $F(c_{01})$  were known, that of  $f(c_{\text{NO}_3})$  would at once be found, at least approximately, since  $\phi(c_{01})$  is roughly equal to  $Kc_1^2$ .

Any such formulation would be, however, of little interest, even

if the assumptions involved were well-founded, unless the form of the function  $f(\text{CNO}_3)$  could be reconciled with some probable (or at least possible) mode of reaction between the constituents. It has not, however, been found possible to find any hypothesis which yields an equation of the form given by the experimental results. Even the assumption that the primary reaction determining the speed is one between silver and iodine ions will not apparently explain the observed results.

This constancy of the bimolecular velocity-coefficient in any particular case, and its variation with change of initial concentration have been observed also by Hecht, Conrad, and Brückner in the case of the ether-formation already mentioned (*Zeit. physikal. Chem.*, 1890, 5, 289). Calling  $v$  the reciprocal of the initial equivalent concentration of the reaction-mixture, they found their results were well represented by the formula  $k_n = k_1 + a \log v$ , where  $a$  is independent of concentration. Suspecting that the cause might be the influence of the reaction products (ether and sodium iodide), they made experiments in which certain amounts of these were added to the reaction-mixture from the start, but found that the velocity-coefficients were not appreciably affected. They also found in different experiments, in which the initial alkyloxide concentration was the same, but the initial alkyl iodide concentration varied, the same value for the velocity-coefficient, showing that the variation in  $k$  must be due to changes in the molecular condition of the alkyloxide. In fact, they give numbers which support the view that the increase of  $k$  with increasing dilution would seem to point to an electrolytic dissociation of the alkyloxide. The reaction has been discussed from the ionic standpoint by Steger (*Rec. trav. chim.*, 1899, 18, 13).

On the supposition that  $\text{C}_2\text{H}_5 \cdot \text{ONa}$  is dissociated into  $\text{C}_2\text{H}_5 \cdot \bar{\text{O}}$  and  $\text{Na}^+$ , and that it is the  $\text{C}_2\text{H}_5 \cdot \bar{\text{O}}$  ions which react to form ether, the constancy of  $k$  in any particular case can be explained, provided the assumption is made that the sodium iodide is dissociated to the same extent as the sodium ethoxide. Steger quotes the results of conductivity experiments obtained by Carrara (*Gazzetta*, 1896, 26, i, 119) which support this assumption.

If the reaction is one of ionic nature, as supposed by Steger, it should follow that the velocity-coefficient would be diminished by adding sodium iodide to the reacting mixture, contrary to the results obtained by Hecht, Conrad, and Brückner. Steger, however, shows that by working in more dilute solution, the velocity-coefficient is actually diminished by the addition of sodium iodide.

Taking all these facts into account, there is therefore considerable qualitative evidence that the ionisation of the alkyloxide plays an

essential part in the reaction. The question cannot, however, be regarded as settled yet, nor is the matter by any means so simple as might appear from the above remarks.

The anomalies observed in the case of ether-formation from alkyl-oxide and alkyl iodide are in so many respects similar to those which occur in the reaction between silver nitrate and ethyl iodide that a discussion of the validity of Steger's theory is of extreme importance. Now Steger's theory necessarily involves some assumption as to the law obeyed by the ionisation of salts in absolute alcohol. In the first instance, it is assumed that the ordinary law of mass action holds good. The reaction, the velocity of which determines the speed, is

$$\text{C}_2\text{H}_5\cdot\bar{\text{O}} + \text{C}_2\text{H}_5\text{I} = \text{C}_2\text{H}_5\cdot\text{O}\cdot\text{C}_2\text{H}_5 + \bar{\text{I}}^*$$

The ionic equilibria,

$$\text{Na}^+ + \text{C}_2\text{H}_5\cdot\bar{\text{O}} = \text{C}_2\text{H}_5\cdot\text{ONa} \quad \text{and} \quad \text{Na}^+ + \bar{\text{I}} = \text{NaI},$$

being supposed to readjust themselves with relatively very great velocity, lead to the equations:

$$kc_u = c_{\text{Na}} \cdot c_{\text{OEt}} \dots\dots\dots (1)$$

$$kc'_u = c_{\text{Na}} \cdot c_{\text{I}} \dots\dots\dots (2)$$

where  $c_u$  = concentration of undissociated sodium ethoxide

$c'_u$  = " " " " sodium iodide.

The condition of electrical equivalence gives the equation

$$c_{\text{I}} + c_{\text{OEt}} = c_{\text{Na}} \dots\dots\dots (3)$$

Denoting by  $c_i$  the initial concentration of total ethoxide,

$$c_u + c'_u + c_{\text{Na}} = c_i \dots\dots\dots (4)$$

Denoting by  $c_s$  the total quantity of ethoxide at any moment (as determined by titration with acid),

$$c_u + c_{\text{OEt}} = c_s \dots\dots\dots (5)$$

$$\text{From (1), (2), and (3), } c_u + c'_u = \frac{c_{\text{Na}}^2}{k}.$$

Substituting in (4), one obtains  $c_{\text{Na}}^2 + kc_{\text{Na}} = kc_i$ ,

$$\text{whence } c_{\text{Na}} = \frac{1}{2}(\sqrt{4kc_i + k^2} - k) \dots\dots (6)$$

\* By writing the reaction equation in this form, we avoid any assumption as to a possible ionisation of the ethyl iodide. Such an ionisation may occur, but there is not as yet any experimental proof of it (compare Lobry de Bruyn and A. Steger, *Rec. trav. chim.*, 1899, 18, 325).

From (1) and (5),

$$c_s = c_{\text{OEt}} + \frac{c_{\text{Na}} \cdot c_{\text{OEt}}}{k}$$

Substituting in this equation the value of  $c_{\text{Na}}$  from (6), the following

$$\text{equation is obtained: } c_{\text{OEt}} = 1 + \frac{2c_s}{\sqrt{1 + 4c_i/k}} \dots\dots\dots (7)$$

It follows from (7) that in any particular reaction, that is, for any given value of  $c_i$ , the ratio  $c_{\text{OEt}}/c_s$  remains constant. It also follows that the smaller is  $c_i$  the greater will be the value of  $c_{\text{OEt}}$  for any given value of  $c_s$ .

The velocity of the reaction may now be considered. As  $\text{C}_2\text{H}_5\text{O}^-$  and  $\text{C}_2\text{H}_5\text{I}$  are the reacting constituents, the fundamental velocity-

$$\text{equation will be } -\frac{dc_{\text{OEt}}}{dt} = Kc_{\text{OEt}} \cdot c_{\text{EtI}} \dots\dots\dots (8)$$

This transforms, however, by means of (7) into

$$-\frac{dc_s}{dt} = Kc_s \cdot c_{\text{EtI}} \dots\dots\dots (9)$$

Equation (9) expresses the velocity in terms of the quantities which are actually measured.\* But since its velocity-coefficient does not involve  $c_i$ , it cannot explain the observed facts. Hence the ionic theory of the reaction proposed by Steger does not lead any further towards an explanation, if the form of the equation of equilibrium given by the ordinary law of mass action is assumed.

The question then arises as to whether any form of the equation of equilibrium would satisfy the requirements of the case.

In order that equation (8) should transform into an equation of the form (9), it is clearly necessary that

$$\frac{d \log c_{\text{OEt}}}{dt} = \phi_1(k, c_i) \frac{d \log c_s}{dt},$$

the solution of which is

$$c_{\text{OEt}} = c_s^{\phi_1(k, c_i)} \cdot \phi_2(k, c_i) \dots\dots\dots (10)$$

If this relation holds, then (8) transforms into

$$-\frac{dc_s}{dt} = \frac{K}{\phi_1} \cdot c_s c_{\text{EtI}} \dots\dots\dots (11)$$

\* Since, in determining total dissolved ethoxide by titration with hydrochloric acid, the reaction occurring is  $\text{EtO}^- + \text{H}^+ = \text{EtOH}$ ,

Equation (11) is not necessarily incompatible with the observed facts. Hence any law of equilibrium leading to a relation between  $c_{\text{OEt}}$  and  $c_s$  of the form (10) (provided  $\phi_1$  does not reduce to a constant) might possibly explain the given facts. According to the results of Hecht,

Conrad, and Brückner,  $\frac{K}{\phi_1} = k' + a \log v = k' - a \log c_i$ , hence one

can write  $\phi = \frac{a}{b - c \log c_i}$  where  $a$ ,  $b$ , and  $c$  are independent of concentration. The relation between  $c_s$  and  $c_{\text{OEt}}$  must then have the form

$$c_{\text{OEt}} = c_s^{\frac{a}{b - c \log c_i}} \cdot \phi_2(c_i).$$

It is possible that some of the newer forms of the equations of ionic equilibrium (compare Nernst, *Zeit. physikal. Chem.*, 1901, 38, 487) might lead to a relation of this sort, but it does not seem very probable. As the molecular conductivities of sodium ethoxide in alcohol have been measured by Tijmstra (*Proc. Roy. Acad. Sci. Amsterdam*, 1903, 104) and those of sodium iodide in alcohol by Völlmer (*Wied. Annalen*, 1894, 52, 328), the material for such a calculation is available.

When we attempt to apply a similar ionic explanation to the reaction between the alkyl iodides and silver nitrate, we are met by still more serious difficulties. In this case, the velocity-coefficient decreases with diminishing initial concentration, whereas it increases in the case of ether-formation. And this occurs notwithstanding the fact that the molecular conductivity of silver nitrate dissolved in ethyl alcohol increases with diminishing concentration, as shown by Völlmer (*loc. cit.*).

The decrease of the velocity-coefficient with decrease of initial concentration might suggest the idea that it is the undissociated silver nitrate molecules which take part in the primary reaction. Völlmer found that the molecular conductivity of solutions of silver nitrate in alcohol could be represented by the formula

$$\lambda_c = a / (1 + \beta c^{\frac{1}{2}} + \gamma c^{\frac{3}{2}}),$$

where  $a = 354$ ;  $\beta = -0.443$ ;  $\gamma = 26.3$ ; and  $c$  = concentration in gram-molecules per litre.

Assuming that the ratio  $\lambda_c/\lambda_0$  gives a measure of the dissociation  $x$ , it follows from Völlmer's formula that

$$x = \frac{1}{1 + \beta c^{\frac{1}{2}} + \lambda c^{\frac{3}{2}}}$$

and hence

$$1 - x = \frac{\beta c^{\frac{1}{2}} + \lambda c^{\frac{3}{2}}}{1 + \beta c^{\frac{1}{2}} + \lambda c^{\frac{3}{2}}}$$

$$\text{and} \quad c(1-x) = \frac{\beta c^{\frac{1}{2}} + \lambda c^{\frac{5}{2}}}{1 + \beta c^{\frac{1}{2}} + \lambda c^{\frac{5}{2}}}.$$

On making this calculation, it will be found that the values of  $c(1-x)$  (the initial concentration of undissociated silver nitrate) for the  $N/20$ ,  $N/40$ , and  $N/80$  solutions, that is, for the values  $c=0.05$ ,  $c=0.025$ , and  $c=0.0125$ , are proportional to the numbers 0.773, 0.3397, and 0.1419. These numbers are, however, very far from being proportional to the corresponding velocity-coefficients, 0.00342, 0.00220, and 0.00139. A weak point in the above argument lies, however, in the assumption  $x=\lambda_c/\lambda_0$ . All that can be said, therefore, is that it has not been found possible as yet to explain the abnormal results obtained by arguments derived from the theory of electrolytic dissociation.

Moreover, as it has not been possible to elucidate the inner mechanism of the reaction, the experimental results do not necessarily justify the view that the reaction is a chemically bimolecular one. The formula \*

$$n = \log \frac{t_2 - t_{02}}{t_1 - t_{01}} / \log \frac{c_{01}}{c_{02}},$$

where  $n$  = order of the reaction;  $c_{01}$ ,  $c_{02}$  = initial concentrations of two equivalent reaction-mixtures;  $t_{01}$ ,  $t_{02}$  = corresponding initial times;  $t_1$ ,  $t_2$  = times at which the same proportionate change has taken place in each solution, cannot be employed here, since the velocity-coefficient is a function of the initial concentration. For example, if the time-concentration curves for  $N/40$  and  $N/80$  equivalent solutions be plotted, they will be found to cross each other.†

In order to ascertain how far the presence of small quantities of water might exert a disturbing effect on the numbers obtained, a special experiment was made with a composite solvent consisting of alcohol (90 per cent.) and water (10 per cent.). The results are given in Table 23.

\* It may be remarked that if this formula is nevertheless applied to the time-concentration curves for  $N/40$  and  $N/80$  equivalent solutions, it gives  $n=2.4$  for the case of ethyl iodide and  $n=2.3$  to  $n=2.6$  for the case of  $n$ -butyl iodide (mean value,  $n=2.47$ ).

† In view of the negative nature of the above result, it may be worth while to point out that, although we have not succeeded in elucidating the mechanism of the reaction, the final products of the reaction may be explained just as well by the following equations as by Nef's theory: (a)  $C_2H_5 \cdot OH = C_2H_5 \cdot \bar{O} + \bar{H}^+$ , (b)  $C_2H_5 \cdot \bar{O} + C_2H_5I = C_2H_5 \cdot O \cdot C_2H_5 + \bar{I}^+$ , (c)  $\bar{Ag} + \bar{I} = AgI$ .

TABLE 23.  $N/40$   $C_2H_5I$ ;  $N/40$   $AgNO_3$ ; ethyl alcohol, 90 per cent.; water, 10 per cent.

Time.	Concentration of $AgNO_3$ .	Value of $k$ .
0·25	15·00	—
10·25	11·30	0·00212
21·00	8·70	0·00229
39·25	6·35	0·00231
59·00	4·75	0·00243
86·00	3·50	0·00254
141·50	2·40	0·00247

---


$$\text{Mean} = 0\cdot00236$$

The mean value for absolute alcohol at the same temperature is 0·00220. We see, therefore, that 10 per cent. of water produces only a comparatively small increase in the value of  $k$ . There is no fear, therefore, of the results communicated in this paper having been modified by the entrance of small quantities of water into the stock of dehydrated alcohol employed for the experiments.

In this connection, another experiment was made in order to determine the effect produced on the velocity of the reaction by the addition of 10 per cent. of dry benzene (Table 24).

Table 24.  $N/40$   $C_2H_5I$ ;  $N/40$   $AgNO_3$ ; ethyl alcohol, 90 per cent., benzene, 10 per cent.

Time.	Concentration of $AgNO_3$ .	Value of $k$ .
0	15·00	—
10·00	11·35	0·00214
12·00	11·10	0·00195
20·00	9·50	0·00193
36·00	7·00	0·00211
56·25	5·75	0·00190
80·75	4·15	0·00215
117·00	3·20	0·00210

---


$$\text{Mean} = 0\cdot00205$$

The non-dissociating solvent, benzene, thus produces a decrease in the value of  $k$ .

As remarked previously, the reaction-mixture always became strongly acid during the experiments recorded in this paper. According to Nef, this acid is nitric, but Chiminello implies that acetic acid is formed. As the present experiments were carried out at a much lower

temperature and with much more dilute solutions than those of Nef, it was considered advisable to ascertain whether the products of reaction were substantially those described by him. It may be said at once that such was found to be the case.

A large volume of an equivalent  $N/20$  mixture of ethyl iodide and silver nitrate in dry ethyl alcohol was prepared and allowed to remain in the thermostat at  $24.5^{\circ}$  until all the silver was precipitated. On opening the flask, a strong odour of ether was apparent, and the presence of a very small trace of aldehyde could be detected by Schiff's reagent. As no acid except nitric could be found by qualitative tests, 200 c.c. of the filtered solution were neutralised with sodium hydroxide, and the solution evaporated to dryness. A careful examination of the residue failed to detect the presence of acetate.

Thirty c.c. of the filtered reaction-mixture required 10.5 c.c. of  $N/10$  sodium carbonate solution for neutralisation (using methyl-orange).<sup>\*</sup> On the assumption that this acidity is all due to nitric acid, it follows that 70 per cent. of the "theoretical" amount of ethyl nitrate must exist as nitric acid (and ordinary ether).

The quantitative estimation of this nitric acid was then made in the following manner: 200 c.c. of the filtered alcoholic solution were shaken with an excess of dry barium carbonate, until the solution ceased to be acid towards methyl-orange. The precipitated barium salts were filtered off, washed with absolute alcohol, and then treated with boiling water and the barium carbonate collected. The aqueous filtrate and washings were then evaporated to dryness in a weighed platinum basin. In this way, 0.9162 gram of barium salt was obtained, which agrees well with 0.9142, the quantity of barium nitrate calculated from the acidity of the solution. The barium salt thus produced was then decomposed in the nitrometer with mercury and strong sulphuric acid, and found to correspond with 99 per cent. of barium nitrate as compared with a control experiment with the pure recrystallised nitrate.

In order to prove the presence of ethyl nitrate in the reaction-mixture, about 450 c.c. were neutralised with solid barium carbonate, filtered, and distilled; the first fraction had a strong odour of ether, whilst the last, after saponification with caustic potash, was found to contain potassium nitrate. No appreciable residue remained in the distilling flask, thus proving the absence of any barium salt soluble in alcohol which might have been formed from the free acid. It is thus conclusively shown that nitric acid is the only acid produced under the conditions of the experiments described in this paper, the other products being ether, ethyl nitrate, and a trace of aldehyde.

<sup>\*</sup> Neither a sharp end-point nor concordant results could be obtained by using barium hydroxide solution and phenolphthalein.

*Summary of Conclusions.*

The main conclusions arrived at in this paper may be summarised as follows :

1. The reaction between silver nitrate and an alkyl iodide in absolute alcohol at  $25.4^{\circ}$  and at concentrations varying from  $N/20$  to  $N/80$  can be expressed by a special form of the bimolecular velocity-equation, in which the velocity-coefficient is a function of the initial concentrations of the reacting components.

2. It is found that in solutions containing the reagents in equivalent amounts, the velocity-coefficient  $k$  increases with the initial molecular concentration  $c$ , the relation between  $k$  and  $c$  being  $k = Kc^{0.53}$ , where  $K$  is independent of concentration.

3. This variation of  $k$  is chiefly due to the silver nitrate. For solutions containing the same  $N/40$  initial concentration of ethyl iodide, and varying ( $N/20$  to  $N/80$ ) initial concentration  $c$  of silver nitrate, the relation between  $k$  and the latter is approximately  $k = Kc^3$ . For solutions containing the same initial concentration of silver nitrate, and varying initial concentration of ethyl iodide, the value of  $k$  decreases as the latter increases, but the rate of decrease is relatively small as compared with the rate of increase produced by silver nitrate.

4. It has not been found possible to explain the variation of  $k$  referred to in 1, 2, and 3. In particular, the assumption that it is the silver ions which take part in the fundamental reaction which regulates the speed does not appear to offer a simple explanation.

5. Similar anomalies have been observed by Hecht, Conrad, and Brückner in the case of ether-formation from sodium alkyloxide and alkyl iodide in alcoholic solution, but the explanation of these anomalies proposed by Steger, based on assumptions concerning the ionisation of the sodium alkyloxide and alkyl iodide in alcoholic solution, does not appear to hold good if the ordinary law of equilibrium is assumed.

6. The theory of alkylene and alkylidene dissociation of the alkyl iodides, proposed by Nef, does not appear to give a satisfactory account of the observed results.

7. The only acid produced in the reaction is nitric, as stated by Nef. Chiminello's statement that acetic acid is formed appears to be incorrect. The other products of the reaction are ether and alkyl nitrate, as stated by Nef.

8. If the reactivities of the alkyl iodides are measured by the velocity-coefficients of the reaction with silver nitrate in absolute alcohol ( $N/40$  equivalent solutions at  $24.5^{\circ}$ ), the order (beginning

with the greatest) is *isopropyl*, *ethyl*, *n-propyl*, *methyl*, *n-butyl*, *isoamyl*, *isobutyl*.

9. This order of reactivities corresponds with the rate of production of free iodine in the alcoholic solutions when exposed to air and light, with the single exception of methyl iodide, the solution of which becomes discoloured at a rate between those of *isopropyl* and *ethyl* iodides.

10. The relative reactivities referred to in (8) do not agree in many respects with those observed in other reactions which have been studied kinetically, such as the reactions with *ethyl sodioacetoacetate* (Wislicenus), *triethylamine* (Menschutkin), *sodium alkyl oxide* (Hecht, Conrad, and Brückner). Compared with these results, *isopropyl iodide* reacts with abnormally great, *methyl iodide* with abnormally small velocity. It does not appear possible, therefore, to ascribe the reactivity of the alkyl haloids to any uniform cause (such, for example, as a dissociation, whether "alkylidene," "alkylene," or electrolytic).

11. So far as the final products and not the kinetics of the reaction are concerned, the production of ether and nitric acid can be accounted for by ionic reactions just as well as by Nef's hypothesis.

The experiments described in this paper are being extended in several directions, for example, to other alkyl and aryl iodides and bromides, and especially to solutions of the alkyl haloids in composite solvents, such as aqueous alcohol.

In conclusion, our best thanks are due to Professor Sir William Ramsay, who suggested the research and whose valuable advice and assistance were constantly at our disposal.

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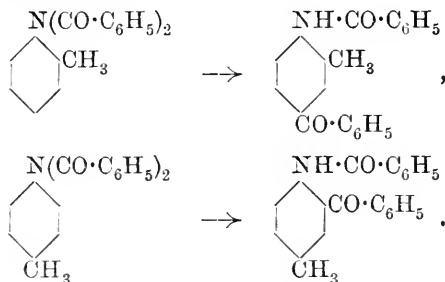
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LVII.—*Isomeric Change of Diacylanilides into Acyl-aminoketones. Transformation of the Dibenzoyl-toluidines into the Isomeric Benzoylaminomethylbenzophenones.*

By FREDERICK DANIEL CHATTAWAY and WILLIAM HENRY LEWIS.

It has been shown recently (this vol., p. 386) that acyl groups must be included among those which, under suitable conditions, can pass from the nitrogen of an aromatic amine into the nucleus, thereby displacing a hydrogen atom in a para- or an ortho-position relatively to the nitrogen.

An excellent illustration of this intramolecular rearrangement in the diacylanilides is furnished by the behaviour of the dibenzoyl-toluidines, which, at a high temperature under the influence of hydrogen chloride, are converted into the isomeric benzoylamino-methylbenzophenones, thus :

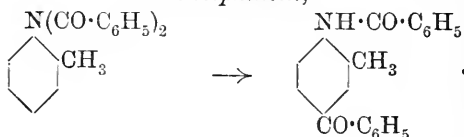


In the transformation of dibenzoyl-*o*-toluidine, where a para- and an ortho-position are unoccupied, the benzoyl group apparently takes up exclusively a para-position with respect to the nitrogen, whilst in the transformation of dibenzoyl-*p*-toluidine an ortho-position is assumed, this being the only vacant position into which the migrating group can enter.

As in the analogous intramolecular rearrangement of the acylchloroamines, interchange between a para-hydrogen atom and the acyl group takes place more readily than that in which an ortho-hydrogen is concerned.

The properties of the aminomethylbenzophenones produced are exactly those which might have been predicted from our knowledge of the properties of the *o*- and *p*-aminobenzophenones obtained by the intramolecular rearrangement of dibenzoylaniline. For example, the compound in which the benzoyl group occupies the ortho-position relatively to the nitrogen has a bright yellow colour, is volatile in steam, and has a low melting point, whilst the isomeride in which the benzoyl group is in the para-position is almost colourless, is not volatile in steam, and melts at a much higher temperature.

*Transformation of Dibenzoyl-o-toluidine into Benzoyl-4-amino-5-methylbenzophenone,*



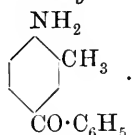
The authors have proved that when the benzoyl derivative of either *o*- or *p*-toluidine is heated with benzoyl chloride, the hydrogen chloride

formed being removed, the dibenzoyl derivative of the base is produced. It is unnecessary, however, to isolate these derivatives in order to study their transformation, as the hydrogen chloride acts as a catalyst and brings about the intramolecular rearrangement. The following procedure gave a good result.

*o*-Toluidine (1 mol.) was added gradually to the equivalent quantity of benzoyl chloride (2 mols.) and the whole gradually heated in an oil-bath up to 220—230°, this temperature being maintained for about 15 hours. A brown, viscid liquid was produced, which solidified on cooling to a hard, resinous mass. The benzoyl-4-amino-3-methylbenzophenone can be isolated from this product with some difficulty, but it is best to hydrolyse it, as the corresponding base can be much more readily separated. The whole mass was therefore dissolved in excess of alcohol containing about half its bulk of concentrated hydrochloric acid, and heated to boiling for 14 hours. A rapid current of steam was then blown through the liquid, when alcohol and ethyl benzoate distilled over successively. The strongly acid residue was then boiled for some time with a quantity of water, and the hot solution containing the hydrochlorides of the bases present filtered from the brown, tarry matter which is always formed in considerable amount in the transformation. The filtrate was next made slightly alkaline with caustic soda and again distilled in steam. A little *o*-toluidine (about 10 per cent. of that used), derived from untransformed dibenzoyl-*o*-toluidine, first passed over. On continuing the distillation, a perfectly colourless\* distillate was obtained, showing that no appreciable transference of the benzoyl group into the vacant ortho-position had taken place. After cooling, the solid separating from the alkaline liquid in the distillation flask was filtered off and extracted with alcohol. This alcoholic solution was evaporated to a small bulk, and a few drops of strong sulphuric acid added; on diluting with a little ether, the almost pure base crystallised in colourless needles. It can be obtained perfectly pure by one recrystallisation from water slightly acidified with sulphuric acid. The yield, which is about 50 per cent. of the weight of *o*-toluidine used, can be slightly increased by adding a small quantity of dry powdered zinc chloride to the mixture of benzoyl chloride and *o*-toluidine before heating.

\* A brilliant yellow colour and volatility in steam are among the most characteristic properties of *o*-aminobenzophenone and its homologues, and a very small quantity of these ketones can be recognised by the yellow colour of the distillate.

## 4-Amino-3-methylbenzophenone,



This compound is very sparingly soluble in hot water, but readily so in alcohol; it crystallises from boiling water in glistening, transparent, flattened prisms, almost colourless, but showing a faint yellow tint. The hot aqueous solution shows a distinct pale yellow colour. From its solution in alcohol, which has a deep yellow colour, the base separates in very pale yellow, flattened prisms with domed ends; it melts at  $112^\circ$ .

0.2224 gave 0.6502  $\text{CO}_2$  and 0.1244  $\text{H}_2\text{O}$ .  $\text{C} = 79.73$ ;  $\text{H} = 6.26$ .

0.3016 „ 17.6 c.c. nitrogen at  $15^\circ$  and 732 mm.  $\text{N} = 6.69$ .

$\text{C}_{14}\text{H}_{13}\text{ON}$  requires  $\text{C} = 79.57$ ;  $\text{H} = 6.21$ ;  $\text{N} = 6.65$  per cent.

The base readily dissolves in hot dilute sulphuric acid, forming a sparingly soluble sulphate,  $2\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{C}_6\text{H}_3(\text{CH}_3) \cdot \text{NH}_2, \text{H}_2\text{SO}_4$ , which crystallises out on cooling the solution in glistening, transparent, colourless plates. When heated rapidly, the sulphate softens and begins to decompose at about  $105$ — $110^\circ$ .

0.2663 yielded 0.1192  $\text{BaSO}_4$ .  $\text{SO}_4 = 18.42$ .

$2\text{C}_{14}\text{H}_{13}\text{ON}, \text{H}_2\text{SO}_4$  requires  $\text{SO}_4 = 18.46$  per cent.

It also dissolves readily in warm concentrated hydrochloric acid, forming a sparingly soluble chloride,  $\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{C}_6\text{H}_3(\text{CH}_3) \cdot \text{NH}_2, \text{HCl}$ , which crystallises from the cooled solution in thin, colourless, transparent, four-sided plates. On heating rapidly, the chloride reddens strongly, and melts with decomposition at about  $215$ — $220^\circ$ .

0.2624 yielded 0.1520  $\text{AgCl}$ .  $\text{Cl} = 14.32$ .

$\text{C}_{14}\text{H}_{13}\text{ON}, \text{HCl}$  requires  $\text{Cl} = 14.32$  per cent.

A number of derivatives of this base and of its isomeride have been prepared, either by the action of the corresponding acyl chloride or anhydride, or by condensing the base with methyl or ethyl chloro-carbonate. As a rule, equivalent quantities were heated together for a short time on the water-bath, the acid liberated being then removed by warming with a dilute solution of potassium hydrogen carbonate. The solid product was repeatedly crystallised from alcohol. In preparing the acetylchloroamino-derivatives, the acetyl compound was dissolved in alcohol and the solution shaken with a well-cooled slightly acid solution of bleaching powder. To complete the conversion, the

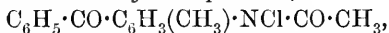
product was extracted with chloroform, and the solution repeatedly shaken with cold, freshly prepared bleaching powder solution slightly acidified with acetic acid. Finally, the chloroform solution was separated, dried over calcium chloride, and the solvent driven off in a current of dry air.

*Acetyl-4-amino-3-methylbenzophenone,*



crystallises from alcohol, in which it is readily soluble in glistening, transparent, flattened rhombs or rhombic plates melting at  $175^\circ$ .

*Acetyl-4-chloroamino-3-methylbenzophenone,*

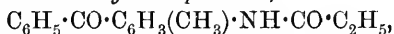


is very soluble in chloroform, but dissolves only sparingly in light petroleum; it crystallises from the latter solvent in small, colourless, slender prisms melting at  $110^\circ$ .

0.2080 liberated I = 14.3 c.c. *N*/10 I. Cl (as NCl) = 12.18.

$\text{C}_{16}\text{H}_{14}\text{O}_2\text{NCl}$  requires Cl (as NCl) = 12.32 per cent.

*Propionyl-4-amino-3-methylbenzophenone,*



is readily soluble in alcohol, from which it crystallises in colourless, silky, needle-shaped crystals (m. p.  $128^\circ$ ).

0.4120 gave 19.2 c.c. nitrogen at  $17^\circ$  and 758 mm. *N* = 5.50.

$\text{C}_{17}\text{H}_{17}\text{O}_2\text{N}$  requires *N* = 5.25 per cent.

*Benzoyl-4-amino-3-methylbenzophenone,*

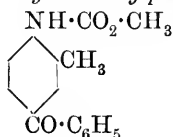


crystallises from alcohol in glistening, colourless, transparent prisms with domed ends which melt at  $158^\circ$ .

0.3632 gave 13.6 c.c. nitrogen at  $16^\circ$  and 752 mm. *N* = 4.40.

$\text{C}_{21}\text{H}_{17}\text{O}_2\text{N}$  requires *N* = 4.45 per cent.

*Methyl 4-Benzoyl-2-methylphenylcarbamate,*



This substance crystallises from alcohol, in which it is very readily soluble, in clusters of transparent, colourless, glistening plates (m. p.  $107^\circ$ ).

0.3051 gave 13.2 c.c. nitrogen at  $14^\circ$  and 756 mm. *N* = 5.14.

$\text{C}_{16}\text{H}_{15}\text{O}_3\text{N}$  requires *N* = 5.22 per cent.

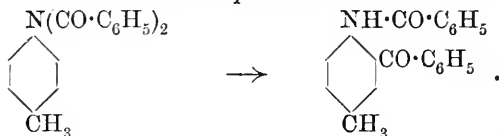
*Ethyl 4-Benzoyl-2-methylphenylcarbamate,*  
 $\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{C}_6\text{H}_3(\text{CH}_3) \cdot \text{NH} \cdot \text{CO}_2 \cdot \text{C}_2\text{H}_5,$

This compound is very soluble in chloroform and alcohol, sparingly so in light petroleum; it crystallises from the latter in small, slender, glistening, transparent, colourless prisms (m. p.  $88^\circ$ ).

0.2480 gave 10.2 c.c. nitrogen at  $15^\circ$  and 758 mm.  $N = 4.88$ .

$\text{C}_{17}\text{H}_{17}\text{O}_3\text{N}$  requires  $N = 4.96$  per cent.

*Transformation of Dibenzoyl-p-toluidine into Benzoyl-2-amino-3-methyl benzophenone.*

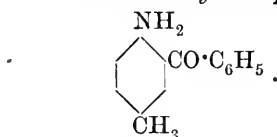


*p*-Toluidine (1 mol.) was added gradually to the equivalent quantity of benzoyl chloride (2 mols.) and the whole gradually heated in an oil-bath to  $220$ — $230^\circ$ , this temperature being maintained for about 15 hours. A brown, viscid liquid was produced which solidified on cooling to a yellowish-brown, semi-crystalline mass; this was hydrolysed by heating for 14 hours with excess of a mixture of alcohol and strong hydrochloric acid, and the alcohol and ethyl benzoate expelled in a rapid current of steam. The acid liquid in the distilling flask was then filtered while hot from the considerable amount of viscid, tarry matter produced, and the latter was several times extracted with boiling dilute hydrochloric acid. The mixed filtrates containing the hydrochlorides of the bases were then made slightly alkaline with caustic soda and again distilled in steam. At first, *p*-toluidine, derived from the untransformed dibenzoyl derivative, passed over; a clear, bright yellow distillate was then obtained from which 2-amino-3-methylbenzophenone separated in deep yellow, oily drops which soon solidified.

The *o*-aminoketone only comes over very slowly in steam, and the distillation must be continued for many hours until the distillate is no longer yellow. The compound is obtained perfectly pure by one crystallisation from alcohol, in which it is very easily soluble. The yield amounts to about 20 per cent. of the weight of *p*-toluidine used. The transference of the benzoyl group from the nitrogen to the ortho-position in the ring does not appear to take place so readily as the corresponding migration into the para-position when the latter is vacant, and resembles in this respect the analogous transference of a

halogen atom. Corresponding with this greater difficulty of transformation, a larger percentage of the toluidine used is recovered, and a larger amount of tarry matter, which appears to be the only other product obtained in the transformation, is also formed. As before, a little zinc chloride may be added with advantage, as this appears to facilitate the transformation.

*2-Amino-3-methylbenzophenone,*



This compound crystallises from alcohol in long, transparent, brilliant yellow, four-sided, rhombic prisms terminated by basal faces. It is very easily soluble in alcohol, chloroform, or acetone, sparingly so in petroleum or water. It is intensely coloured, and a very small quantity gives a distinct pure yellow colour to a large bulk of any solvent. It melts at 66°.

0.2364 gave 0.6884 CO<sub>2</sub> and 0.1320 H<sub>2</sub>O. C = 79.42; H = 6.25.

0.3192 „ 17.8 c.c. nitrogen at 13° and 749 mm. N = 6.59.

C<sub>14</sub>H<sub>13</sub>ON requires C = 79.57; H = 6.21; N = 6.65 per cent.

The base dissolves readily in dilute sulphuric acid, forming a colourless, very soluble sulphate. It also dissolves easily in warm dilute hydrochloric acid, forming a colourless solution from which the hydrochloride C<sub>6</sub>H<sub>5</sub>·CO·C<sub>6</sub>H<sub>3</sub>(CH<sub>3</sub>)·NH<sub>2</sub>·HCl separates on cooling in colourless, transparent, flattened prisms which partially decompose and become yellow on washing with water or alcohol, owing to the liberation of the base, but are permanent in dry air. The hydrochloride, when heated rapidly, reddens and melts with decomposition at about 195—197°.

0.3400 gave 0.1988 AgCl. Cl = 14.46.

C<sub>14</sub>H<sub>13</sub>ON, HCl requires Cl = 14.32 per cent.

*Acetyl-2-amino-3-methylbenzophenone,*

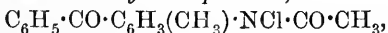


crystallises from alcohol in large, colourless, four-sided, rhombic plates (m. p. 159°).

0.2259 gave 10.7 c.c. nitrogen at 13° and 752 mm. N = 5.62.

C<sub>16</sub>H<sub>15</sub>O<sub>2</sub>N requires N = 5.55 per cent.

*Acetyl-2-chloroamino-5-methylbenzophenone,*



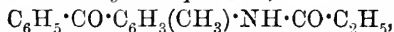
is very soluble in chloroform, moderately so in warm light petroleum,

from which it crystallises in colourless, transparent, four-sided plates (m. p. 116°).

0.2668 liberated I = 18.7 c.c. N/10 I. Cl (as NCl) = 12.42.

$C_{16}H_{14}O_2NCl$  requires Cl (as NCl) = 12.32 per cent.

*Propionyl-2-amino-5-methylbenzophenone,*



is very readily soluble in alcohol, and crystallises from it in transparent, colourless, rhombic plates (m. p. 99°).

0.3535 gave 16.1 c.c. nitrogen at 16° and 762 mm. N = 5.42.

$C_{17}H_{17}O_2N$  requires N = 5.25 per cent.

*Benzoyl-2-amino-5-methylbenzophenone,*



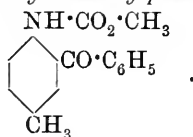
is moderately soluble in alcohol, from which it crystallises in long, slender, very pale yellow prisms (m. p. 118°).

0.2706 gave 10.5 c.c. nitrogen at 17° and 755 mm. N = 4.56.

$C_{21}H_{17}O_2N$  requires N = 4.45 per cent.

All the acyl derivatives of 2-amino-5-methylbenzophenone give yellow solutions, but only the benzoyl derivative shows any yellow tint in the crystalline form.

*Methyl 2-Benzoyl-4-methylphenylcarbamate,*



This ester crystallises from alcohol, in which it is readily soluble, in colourless, transparent, rhombic plates (m. p. 110°).

0.3132 gave 13.6 c.c. nitrogen at 14° and 752 mm. N = 5.13.

$C_{16}H_{15}O_3N$  requires N = 5.22 per cent.

*Ethyl 2-Benzoyl-4-methylphenylcarbamate,*



This compound is very soluble in chloroform, alcohol or light petroleum; from the last of these solvents it crystallises in transparent, very pale yellow, four-sided prisms (m. p. 58°).

0.2576 gave 10.4 c.c. nitrogen at 18° and 758 mm. N = 4.74.

$C_{17}H_{17}O_3N$  requires N = 4.96 per cent.

LVIII.—*Estimation of Hydrogen Peroxide in the presence of Potassium Persulphate by means of Potassium Permanganate.*

By JOHN ALBERT NEWTON FRIEND, M.Sc.

WHILE Dr. Price and I were engaged in investigating Caro's acid, we noticed that hydrogen peroxide could not be correctly estimated by titration with potassium permanganate when this acid was present. The amount of permanganate required always fell short of the theoretical amount (compare Price, Trans., 1903, 83, 546).

Since we obtained Caro's acid by the action of strong sulphuric acid on potassium persulphate, it was natural to inquire whether the potassium persulphate itself might not act in a similar manner. At the suggestion of Dr. Price, whom I take this opportunity of thanking, I have investigated the subject, and my results show that, in ordinary circumstances, a correct estimate of the hydrogen peroxide is not obtained by titration with potassium permanganate when potassium persulphate is present. This fact has an important bearing on much of the work done in connection with persulphates, as many investigators have used this method for the estimation of hydrogen peroxide, believing it to be trustworthy.

In the sequel,  $N/50$  permanganate was used, except where otherwise indicated. The potassium persulphate was recrystallised and free from sulphate; the hydrogen peroxide was obtained from Merck, and guaranteed pure. All the experiments were conducted at the ordinary temperature.

1. *Time of Titration.*

It was found that the amount of permanganate varied considerably with the rate at which it was poured from the burette into the mixture of hydrogen peroxide and potassium persulphate solutions. In each of the following series, the volume titrated and the amounts of hydrogen peroxide, potassium persulphate, and sulphuric acid present were constant throughout, but the rapidity with which the titrations were effected was varied.

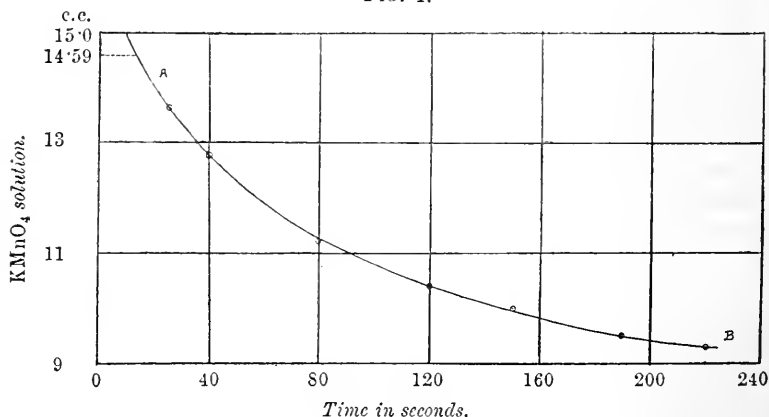
Series I. $m/85 \text{ K}_2\text{S}_2\text{O}_8$ .		Series II. $m/102 \text{ K}_2\text{S}_2\text{O}_8$ .	
Time of titration.	Titre in c.c. $\text{KMnO}_4$ .	Time of titration.	Titre in c.c. $\text{KMnO}_4$ .
25 secs.	13.63	5 secs.	11.00
40 "	12.78	10 "	10.87
80 "	11.22	20 "	10.78
120 "	10.42	40 "	10.49
150 "	10.02	75 "	10.31
190 "	9.52	95 "	10.30
220 "	9.28	120 "	10.15
theoretical value		theoretical value	
14.59		11.00	

Series III. $m/102 \text{ K}_2\text{S}_2\text{O}_8$ .		Series IV. $m/136 \text{ K}_2\text{S}_2\text{O}_8$ .	
Time of titration.	Titre in c.c. $\text{KMnO}_4$ .	Time of titration.	Titre in c.c. $\text{KMnO}_4$ .
15 secs.	12.30	0.33 mins.	10.23
20 "	12.20	1.10 "	9.89
30 "	12.09	1.83 "	9.45
60 "	11.03	2.50 "	9.33
90 "	10.65	4.00 "	9.08
150 "	10.50	7.60 "	8.71
theoretical value		theoretical value	
12.26		10.54	

The results of Series I are shown in Fig. 1. If the curve be produced in the direction of *A*, it will not meet the vertical axis at the zero

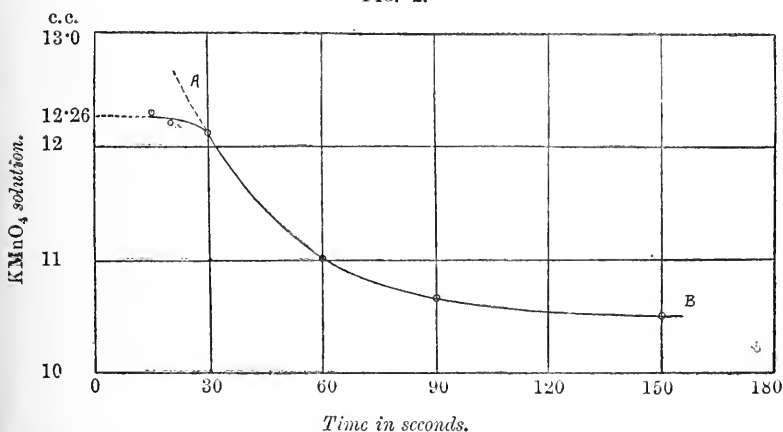
FIG. 1.



of time at a point corresponding with the theoretically correct titration (14.59 c.c.). If, however, very rapid titrations are effected, it is found that the amount of permanganate required does not exceed the theoretical amount. The curve suddenly departs from its original course, becoming nearly parallel to the horizontal axis. This is seen in Fig. 2, which represents the results of Series III. As it is almost impossible to effect a titration of any value in fewer than about 10 seconds, we cannot follow the curve right up to the zero of time.

The results of Series IV show that if the time of titration is greatly prolonged, the amount of permanganate required does not become constant, so that the curve (Figs. 1 and 2) produced in the direction

FIG. 2.



of *B* shows no signs of becoming parallel to the horizontal axis.

It will be clear from the above that if it is desired to compare titrations of different mixtures of hydrogen peroxide and potassium persulphate, the times of titration must be the same. The most convenient interval is perhaps 1 minute, for the curve is then not so steep as for a shorter period, and any slight error in the time of titration causes a smaller experimental error than would otherwise be the case.

In the sequel, all the titrations have been performed during this interval of time.

## 2. Concentration of Persulphate.

In each of the following series, the volume, time of titration, and amount of acid present were kept constant throughout, but the concentration of the potassium persulphate was varied.

In Series VIII, *N*/75 permanganate was employed.

Series VI.*		Series VII.		Series VIII.	
Concentration of $K_2S_2O_8$ .	Titre in c.c. $KMnO_4$ .	Concentration of $K_2S_2O_8$ .	Titre in c.c. $KMnO_4$ .	Concentration of $K_2S_2O_8$ .	Titre in c.c. $KMnO_4$ .
$m/119$	24.73	$m/119$	13.69	$m/85$	11.21
$m/159$	25.40	$m/159$	13.90	$m/122$	12.06
$m/238$	25.80	$m/238$	14.19	$m/189$	12.95
$m/476$	26.63	$m/476$	14.50	$m/283$	13.68
$m/795$	27.02	$m/795$	14.70	$m/425$	14.17
$m/1590$	27.30	$m/1590$	14.90	$m/850$	15.10
$m/3400$	27.50	$m/3400$	15.02	$m/\infty$	16.22
$m/\infty$	27.70	$m/\infty$	15.36	—	—

It is clear from the foregoing tabulation that the greater the amount of potassium persulphate present, the greater is the deviation of the permanganate required from the theoretical amount. This is precisely what one might expect.

### 3. Dilution.

In each of the following series, the amounts of hydrogen peroxide, potassium persulphate, and sulphuric acid were kept constant, as also the time of titration, the volume alone being altered by the addition of distilled water.

Series IX.		Series X.		Series XI.	
Total volume titrated.	Titre in c.c. $KMnO_4$ .	Total volume titrated.	Titre in c.c. $KMnO_4$ .	Total volume titrated.	Titre in c.c. $KMnO_4$ .
20	14.90	20	23.90	20	10.92
25	14.82	25	23.68	25	10.90
30	14.62	30	23.60	30	10.88
35	14.50	35	23.40	35	10.76
45	14.28	45	23.22	45	10.69
55	13.97	55	22.95	55	10.43
70	13.70	70	22.68	70	10.03
90	13.32	—	—	—	—

As the dilution increases, the effect of the potassium persulphate becomes correspondingly greater. It is quite possible that a dissociation of persulphate may account for this.

\* The symbol  $m$  in the tables signifies one gram-molecule of the substance dissolved in one litre of water.

4. Concentration of Sulphuric Acid.

In each of the following series, the volume was kept constant, as also the amounts of persulphate and hydrogen peroxide, and the time of titration, but the quantity of sulphuric acid was varied.

Series XII.  $m/238 \text{ K}_2\text{S}_2\text{O}_8$ .

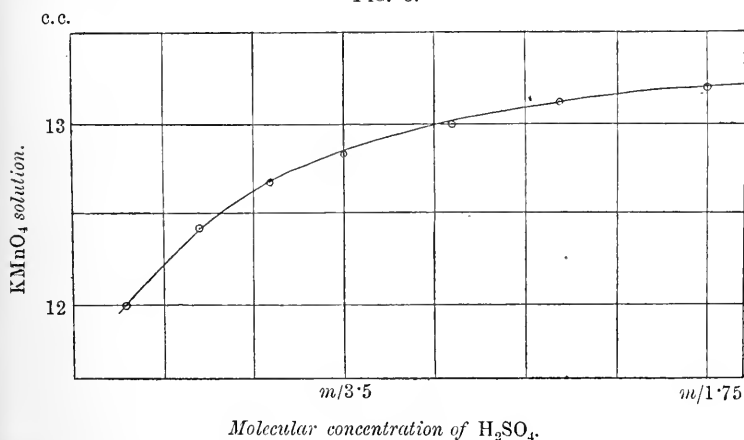
Strength of $\text{H}_2\text{SO}_4$ .	Titre in c.c. $\text{KMnO}_4$ .
$m/8.9$	12.00
$m/5.93$	12.42
$m/4.4$	12.67
$m/3.5$	12.83
$m/2.7$	12.99
$m/2.2$	13.12
$m/1.75$	13.20
Theoretical	13.62

Series XIII.  $m/238 \text{ K}_2\text{S}_2\text{O}_8$ .

Strength of $\text{H}_2\text{SO}_4$ .	Titre in c.c. $\text{KMnO}_4$ .
$m/12$	25.40
$m/7$	25.60
$m/5$	25.77
$m/2.3$	26.52
$m/1.8$	26.88
$m/0.9$	27.23
$m/0.6$	27.20
Theoretical	27.23

The results of Series XII are shown in Fig. 3; this diagram indicates a curve which is exactly opposite to those previously obtained.

FIG. 3.



By increasing the amount of sulphuric acid, the titration approaches more and more nearly to the true value, and indeed finally reaches it if the excess of acid is sufficiently great.

### 5. Estimation of Hydrogen Peroxide.

From the foregoing, it appears that a correct titration might be obtained if attention were paid to the following points.

1. The rapidity with which the titration is effected should be as great as possible.

2. The volume of the solution titrated should be reduced to a minimum.

3. Great excess of sulphuric acid should be employed.

That such is possible will be evident from a consideration of the following results.

Column I gives the volume of the solution titrated.

Columns II and III indicate respectively the molecular strengths of the sulphuric acid and potassium persulphate present in the solution.

Column IV gives the number of c.c. of permanganate required, and Column V the theoretical value, that is, the number which would have been required had no persulphate been present. The time of titration was about 30 seconds.

Volume.	H <sub>2</sub> SO <sub>4</sub> .	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> .	KMnO <sub>4</sub> required.	KMnO <sub>4</sub> . Theoretical value.
25 c.c.	m/1.5	m/170	24.10 c.c.	24.16 c.c.
25	m/1.5	m/170	20.20	20.20
20	m/1.0	m/134	24.10	24.16
20	m/1.0	m/134	20.16	20.20
20	m/1.0	m/134	17.50	17.57
20	m/1.5	m/227	24.13	24.16
20	m/1.5	m/227	20.15	20.20

The above numbers show a moderate agreement, the greatest error being 0.4 per cent.

In a future paper I hope to show the cause of the varying titrations, and to give in more detail the most favourable conditions for effecting a correct titration.

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LIX.—*The Heat of Formation of Glucinum Chloride.*

By JAMES HOLMS POLLOK, B.Sc.

SINCE the discovery of glucinum by Vauquelin in 1798, it has been the subject of numerous researches by many chemists; but so far as I am aware the heat of formation of the glucinum compounds has never been determined; and very little work has been done on the thermo-chemistry of this element, beyond the determination of the heat of neutralisation of hydrofluoric and sulphuric acids by the base.

This research was undertaken with the view of obtaining the heat of formation of the chloride direct from the metal, so as to supply the necessary data for the calculation of the heats of formation of other salts from the heats of neutralisation of the various acids by the base.

1. *Extraction of Glucina from Beryl.*

The sample of beryl procured from Limoges had a pale green colour and consisted of opaque plates or sheets, not showing any signs of hexagonal crystals; it seemed of uniform character, and not contaminated with rock or other minerals. The whole quantity (10 pounds) was disintegrated, mixed, sampled, and a fine sample carefully ground for analysis. The mean results of a number of fairly concordant analyses were as follows:

	Per cent.		Per cent.
Silica .....	64.41	Magnesia .....	0.02
Alumina.....	18.82	Nickel and zinc oxides	0.74
Glucina .....	11.65	Combined water .....	1.22
Lime .....	0.65	Alkali chlorides .....	0.68
Copper .....	a trace		—
Ferrous oxide .....	1.46		99.65

To separate the glucina, 2,000 grams of ground beryl were fused with their own weight of caustic soda, in a large salamander crucible for about one hour, the contents of the crucible then being perfectly liquid. When cold, the fused mass was ground up, treated with excess of strong hydrochloric acid, the whole boiled with steam, and the silica separated on a linen filter and thoroughly washed. The solution was now precipitated by ammonia, and the very bulky precipitate of iron, alumina, and glucina collected, dissolved in hydrochloric acid, and the solution saturated with hydrogen chloride, which precipitates nearly all the aluminium as chloride, but leaves the whole of the iron and glucina in solution. The pre-

cipitated aluminium chloride was filtered at the pump through glass wool and the precipitate washed with concentrated hydrochloric acid. The pure white, crystalline aluminium chloride was easily collected. On boiling off the hydrochloric acid from the solution and concentrating, a reddish-yellow, syrupy solution was obtained, containing the iron and glucina as chlorides. This solution was added in quantities of 100 c.c. at a time to two litres of saturated ammonium carbonate solution, and shaken up in "Winchester quarts." At first, a heavy, curdy precipitate was produced, which, on shaking, redissolved completely to a perfectly clear solution; in about five minutes, this became cloudy, and in ten minutes quite a heavy precipitate separated, this very curious phenomenon being repeated exactly in each vessel. This precipitate consists chiefly of alumina with a little iron and glucina, and about 80 grams were collected for further examination.

The clear solution of glucina in ammonium carbonate was now treated with a few drops of ammonium sulphide and left for two days, when the black precipitate was collected. This precipitate consisted chiefly of iron, zinc, and nickel sulphides, but another substance appeared to be present; its amount was, however, too minute to admit of any satisfactory conclusion being drawn regarding it. This sulphide has also been observed by Kruss and Morah. The ammonium carbonate solution of glucina, now free from silica, alumina, and iron, was boiled and evaporated to about half its bulk, the glucinum being precipitated as a beautiful white basic carbonate containing only a small quantity of alumina. Other experiments were similarly conducted, and I finally obtained more than 800 grams of pure white basic glucinum carbonate.

To purify the basic carbonate, I used the method of fractional solution in ammonium carbonate, the product giving the following numbers on analysis: glucina, 37.9; carbon dioxide, 22.9; and water, 39.2 per cent., these data corresponding with the formula  $\text{GlCO}_3, 2\text{GlH}_2\text{O}_2, 2\text{H}_2\text{O}$ .

A quantity of the purified basic carbonate was dissolved in dilute sulphuric acid and the filtered solution left over sulphuric acid under diminished pressure, when a good crop of large crystals of sulphate was obtained.

On analysis, this salt gave the following data:  $\text{GlO} = 14.34$ ,  $\text{SO}_4 = 46.60$ , and  $\text{H}_2\text{O} = 39.06$  per cent.  $\text{GlSO}_4, 4\text{H}_2\text{O}$  requires  $\text{GlO} = 14.17$ ,  $\text{SO}_4 = 45.17$ , and  $\text{H}_2\text{O} = 40.66$  per cent.

## 2. *Anhydrous Glucinum Chloride.*

A number of preliminary experiments showed that the best method of making anhydrous glucinum chloride was to mix the oxide with four

times its own weight of sugar, and char in a Hessian crucible at a dull red heat; then to place the intimate mixture of carbon and glucina thus formed in a porcelain tube, maintained at a bright red heat in a furnace with a Fletcher burner, and pass a steady stream of perfectly dry chlorine over the heated mass. The chloride formed freely, and condensed in pure white, silky needles at a point just beyond the red-hot zone of the tube, whilst the part next to the tube fused to a white mass. In the earlier experiments, the chloride was yellow, the colour being due to the presence of iron.

In one experiment, 10 grams of glucina ignited with 20 grams of sugar gave 25 grams of anhydrous chloride and 1 gram of unaltered residue, and other experiments gave similar results. Theoretically, 10 grams of dry glucina should yield about 32 grams of anhydrous chloride.

A careful analysis of the chloride gave the following numbers:  $\text{Gl} = 11.87$ ,  $\text{Cl} = 88.13$ , whilst  $\text{GlCl}_2$  requires  $\text{Gl} = 11.38$ ,  $\text{Cl} = 88.62$  per cent.

### 3. *Metallic Glucinum.*

The production of metallic glucinum in a state of reasonable purity was found to be a task of great difficulty. I first tried the electrolytic decomposition of the anhydrous chloride, fused in a test-tube surrounded by the vapour of boiling sulphur, and although not successful as a method of obtaining pure metal, the experiment was interesting, as the jacket of sulphur vapour had just the right temperature to keep the chloride perfectly molten without vaporising any. Evidently glucinum chloride melts at about  $400^\circ$ , and boils at about  $500^\circ$ ; and I cannot understand how Carnelly came to give the melting point as lying between  $585^\circ$  and  $617^\circ$ , and maintained the accuracy of these figures after Nilson and Pettersson had pointed out that the chloride boiled at  $520^\circ$ . There is absolutely no doubt that the anhydrous chloride melts below, and near to, the boiling point of sulphur ( $440^\circ$ ), and that its vapour condenses just below a red heat, as can easily be seen when its preparation is conducted in a glass tube. As a red heat begins somewhere between  $500^\circ$  and  $550^\circ$ , according to the manner in which the observation is made, this agrees very well with Nilson and Pettersson's figure.

After a number of trials, the following method of procedure was adopted:

A piece of sodium was pressed into the bottom of a good-sized nickel crucible, the anhydrous chloride was rapidly introduced, more sodium placed on the top, and the crucible gently heated until the reaction set in. The lid, which was blown off, was quickly replaced, and the crucible plunged into absolute alcohol in order to dissolve out

the excess of sodium, the whole being thoroughly boiled once or twice with fresh portions of absolute alcohol, and then finally washed with hot water. There always seemed to be a good deal of action when the water was first applied, and this was, no doubt, due to the impossibility of completely removing all the sodium hydroxide, and this alkali has a vigorous action on glucinum. After washing, the water had no further action on the metal, even on boiling. The glucinum thus obtained was in the form of a dark grey powder, which assumed a bright grey or white metallic lustre under the burnisher. A nickel crucible is quite unacted on by metallic sodium, and in this way comparatively large quantities may be operated on with safety.

It was hoped that, by using an excess of metallic sodium, crystalline glucinum might be obtained, after the manner employed by Moissan in preparing calcium; but it was found that glucinum did not alloy with sodium. A portion of the metal was analysed by dissolving in hydrochloric acid, the hydrogen evolved being collected and measured; the specimen was found to contain glucinum, 59.16; glucina, 40.84 per cent., and traces only of iron oxide, &c.

#### 4. *The Volatility of Metallic Glucinum.*

An attempt was now made to fuse the glucinum under salt, but without success, although platinum, nickel, and lime crucibles were tried. At a high temperature, the glucinum alloyed with the two former, and with the latter the salt and metal were both volatilised before the latter seemed to melt, but no doubt, if I had taken more pains with this method, and had stopped at the right moment, the experiment might have been successful, as J. E. Reynolds succeeded in producing a small fused mass by this method, although he also noticed a great loss of metal. I then tried the electric arc in an atmosphere of hydrogen, by making a hollow in the end of the positive carbon, surrounded by a small lime cylinder, kept in position by a little copper wire bound round the carbon, and then placing a little of the glucinum powder in the miniature electric furnace thus formed. An ordinary lamp-chimney was corked over the upper and negative carbon and kept full of hydrogen gas. Contact was now made by passing the positive carbon up through the foot of the chimney, when an arc was formed; after a few minutes, the current was switched off, and the carbon and lime crucible allowed to cool in hydrogen. It was found that the glucinum showed no sign of fusion, but on the copper wire bound round the carbon to support the lime jacket there was a film of the metal, which showed that under atmospheric pressure it volatilised without fusion, and this would explain the

great difficulty all investigators have found in producing any large quantity of fused glucinum.

Nilson and Pettersson succeeded in fusing glucinum under salt in some quantity, but they did this under pressure in an iron crucible with the lid screwed down.

### 5. *Thermo-chemical Notation.*

In recording and calculating the results of my experiments I have adopted the notation described in my paper to the Royal Dublin Society, 1899. The solid, liquid, gaseous, and dissolved states are indicated by a dot, dash, T, or circle ( $\cdot$  — T  $^{\circ}$ ) placed under the formula of the substance. The heat of formation of a compound is indicated by  $\xi$  placed before its formula. The heat of a reaction is indicated by enclosing the equation in brackets and placing  $\xi$  before it. The heat evolved in the transition from one state to another is indicated by  $\xi$  with the sign for the initial and final state at the bottom and top respectively, K $^{\circ}$  and k $^{\circ}$  represent kilogram- and gram-degrees of heat. Thus,  $\xi^{\circ}\text{GlCl}_2 = 44\cdot5\text{K}^{\circ}$  indicates that the heat of solution of anhydrous glucinum chloride is 44·5 kilogram-degrees per gram-molecule, whilst  $\xi\text{GlCl}_2 = 155\text{K}^{\circ}$  indicates that the heat of formation of a gram-molecule of solid glucinum chloride is 155 kilogram-degrees.

The expression  $\xi[\overset{\cdot}{\text{Gl}} + 2\overset{\circ}{\text{HCl}} = \overset{\circ}{\text{GlCl}_2} + \overset{\text{T}}{\text{H}_2}] = 121\cdot1\text{K}^{\circ}$  indicates that the heat evolved in the solution of a gram-atom of glucinum in hydrochloric acid is 121·1 kilogram-degrees.

The advantage of this notation over that of Thomsen or Berthelot is that every symbol preceded by the letter  $\xi$  indicates a definite algebraic quantity of heat. The formulæ and equations retain their ordinary chemical interpretation, and all the equations are algebraically correct.

### 6. *Heat of Solution of Glucinum Compounds.*

The heat of solution of anhydrous glucinum chloride was determined by projecting a quantity of the pure dry chloride from a weighing-bottle into a calorimeter of very thin glass, surrounded by an outer glass vessel so as to form an air-jacket. The calorimeter contained 187 c.c. of water, which, together with the thermal equivalent of the beaker, stirrer, and thermometer, was equal to 200 grams of water. The thermometer used was specially made for the experiments, and had a long, thin bulb, equal to the depth of liquid in the beaker, so as to give the rise of temperature quickly with the minimum of stirring, on the principle of Bottomley's integrating thermometer; the stem was

graduated in fiftieths of a degree, from  $10^{\circ}$  to  $30^{\circ}$ , and could easily be read to  $0.01^{\circ}$ .

In the first experiment, 0.845 gram of chloride dropped into the calorimeter dissolved almost instantly, and gave a rise of  $2.26^{\circ}$ . Thomsen has established that, for the purposes of this class of experiment, the heat capacity of a dilute solution may be taken as equal to that of the water; so, multiplying by 200, this gives us 452 gram-degrees per 0.845 gram of anhydrous chloride. Multiplying by 80, and dividing by 0.845, this gives 42.9 kilogram-degrees as the heat of solution of a gram-molecule of anhydrous glucinum chloride. Thus :

$$\frac{0.845}{80.1} \xi^{\circ} \text{GlCl}_2 = 2.26 \frac{\text{K}^{\circ}}{5}. \quad \xi^{\circ} \text{GlCl}_2 = \frac{2.26 \times 80}{0.845 \times 5} \text{K}^{\circ} = 42.9 \text{K}^{\circ}.$$

The advantage of this notation is that the equation can always be written down direct from the experimental figures, without any other explanation whatever. The results of all the experiments may be summarised as follows :

Grams of substance.	Rise of temperature.	Gram-degrees of heat.	Molecular heat of solution.
0.845	$2.26^{\circ}$	452k $^{\circ}$	42.9K $^{\circ}$
1.356	3.80	760	45.0
1.221	3.38	676	44.3
1.332	3.69	738	44.3

Neglecting the first experiment, this gives the mean value of the heat of solution of anhydrous glucinum chloride,

$$\xi^{\circ} \text{GlCl}_2 = 44.5 \text{K}^{\circ}.$$

Ten grams of the sulphate, when dissolved, gave a rise of  $0.24^{\circ}$ , equal to 48 gram-degrees of heat. In a second experiment, 10 grams gave precisely the same result. This gives 0.85 kilogram-degrees for the molecular heat of solution of crystallised glucinum sulphate,

$$\frac{10}{177} \xi^{\circ} \text{GlSO}_4 \cdot 4\text{H}_2\text{O} = 48 \text{k}^{\circ}. \quad \xi^{\circ} \text{GlSO}_4 \cdot 4\text{H}_2\text{O} = 0.85 \text{K}^{\circ}.$$

As anhydrous glucinum chloride dissolves freely in absolute alcohol with great rise of temperature, I thought it would be interesting to determine the molecular heat of solution in this solvent. On projecting 0.724 gram of chloride into 200 c.c. of alcohol and stirring, the temperature rose from  $14.82^{\circ}$  to  $18.00^{\circ}$ , a rise of  $3.18^{\circ}$  in two minutes. A second portion of 0.781 gram projected into the same solution raised the temperature from  $17.56^{\circ}$  to  $20.78^{\circ}$ , a rise of  $3.22^{\circ}$  in two minutes. After cooling for two minutes, the temperature

was  $20.52^{\circ}$ , thus giving a decrement of  $0.26^{\circ}$ . The undissolved residue of carbon from both experiments weighed 0.0955 gram; deducting this, and adding the results of both experiments and half the rate of cooling, we have a rise of  $6.68^{\circ}$  on the solution of 1.41 grams of anhydrous chloride in 200 c.c. of absolute alcohol. The specific heat of alcohol is 0.615, the specific gravity of the sample being 0.801. This gives 37.4 kilogram-degrees for the molecular heat of solution of glucinum chloride in alcohol.

### 7. Heat of Formation of Glucinum Chloride.

For the heat of formation of the chloride, a thin glass globe was used with a spiral to cool the escaping gases, and a small tap-funnel to supply the acid. The globe being immersed in a calorimeter containing a quantity of water such, that this liquid, together with the corrections for the glass of the apparatus, including the thermometer and stirrer and hydrochloric acid added, was just equivalent to one kilogram-degree; so that the thermometer read off in gram-degrees direct, without the necessity of a separate correction for each experiment. Surrounding the calorimeter was an outer vessel to act as an air-jacket.

The thermometer used was similar to that employed for determining the heat of solution, having a long, narrow mercury bulb, of the same length as the depth of liquid in the calorimeter; and the stem was graduated to fiftieths of a degree, and easily read to  $0.01^{\circ}$ .

In each experiment, a quantity of glucinum powder was dropped into the glass globe: 25 c.c. of moderately strong hydrochloric acid were put in the funnel, the acid being as nearly as possible at the same temperature as the water of the calorimeter. The exit from the spiral tube was connected with a pneumatic trough, with a graduated cylinder to collect the hydrogen evolved. When all was ready, the temperatures of the water in the calorimeter, the acid in the funnel, and the air in the outer jacket of the calorimeter were noted. The acid was then run in, the water in the calorimeter well stirred until all action had ceased, and the temperature of the water in the calorimeter again noted. The hydrogen evolved by the reaction was carefully measured and the volume corrected to  $0^{\circ}$  and 760 mm., of course allowing for the 25 c.c. of acid run into the globe. From the volume of hydrogen liberated, the weight of glucinum dissolved in the experiment was calculated.

The details of one of the most satisfactory experiments were as follows: temperature of the air jacket,  $15.5^{\circ}$ ; temperature of the acid,  $15.55^{\circ}$ ; temperature of the water in the calorimeter before the experiment,  $15.54^{\circ}$ ; and after the experiment,  $17.08^{\circ}$ ; rise,  $1.54^{\circ}$ ;

the hydrogen evolved corrected to 0° and 760 mm. measured 277·8 c.c., equal to 0·1157 gram of glucinum. The solution of 0·1157 gram of glucinum therefore evolved 1·54 kilogram-degrees of heat, and on multiplying by 9·1, dividing by 0·1157, and adding 78·6—the heat of formation of hydrochloric acid in solution—we get 199·7 kilogram-degrees for the molecular heat of formation of glucinum chloride in solution. The results may be stated thus :

$$\begin{aligned} \frac{0\cdot1157}{9\cdot1} \xi [\text{Gl} + 2\text{HCl} = \text{GlCl}_2 + \text{H}_2] &= 1\cdot54\text{K}^\circ, \\ - \xi \text{Gl} - 2\xi \text{HCl} + \xi \text{GlCl}_2 + \xi \text{H}_2 &= \frac{1\cdot54 \times 9\cdot1}{0\cdot1157} \text{K}^\circ, \\ \text{O} - 78\cdot6 + \xi \text{GlCl}_2 + \text{O} &= 121\cdot1\text{K}^\circ; \\ \therefore \xi \text{GlCl}_2 &= 199\cdot7\text{K}^\circ. \end{aligned}$$

The results of all the experiments are summarised in the following table :

Glucinum dissolved.	Rise of temperature.	Molecular heat of formation.
0·0920 gram	1·14°	191·4K°
0·0125 „	0·16	195·1 „
0·0333 „	0·50	215·2 „
0·1157 „	1·54	199·7 „
0·0868 „	1·14	189·2 „
0·1543 „	2·07	200·7 „

Taking the average of the last three results, we have, for the heat of formation of glucinum chloride in solution,

$$\xi \text{GlCl}_2 = 199\cdot5\text{K}^\circ;$$

deducting the heat of solution, we get 155 kilogram-degrees for the molecular heat of formation of anhydrous glucinum chloride,

$$\xi \text{GlCl}_2 = 155\cdot0\text{K}^\circ.$$

Comparing these results with the heat of formation and solution of anhydrous aluminium chloride, we have :—

	$\text{Al}_2\text{Cl}_6$ .	$\frac{1}{2}\text{Al}_2\text{Cl}_6$ .	$\text{AlCl}_3$ .
Heat of formation.....	323·6	107·9	155·0
Heat of solution .....	152·6	50·9	44·5

so that for equivalent quantities, the heat of formation of glucinum chloride is much higher than that of aluminium chloride, and the heat of solution somewhat less.

Comparing glucinum, magnesium, and zinc chlorides, we have:—

	GICl	MgCl <sub>2</sub> .	ZnCl <sub>2</sub> .
Heat of formation .....	155·0	151·0	97·4
Heat of solution .....	44·5	36·0	15·6

In each case, a fall in the heats of formation and solution accompanies the rise of atomic weight.

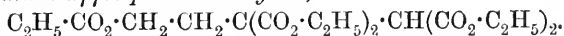
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## LX.—*The Action of Ethyl $\beta$ -Iodopropionate on Ethyl Disodioethanetetracarboxylate.*

By OSWALD SILBERRAD, Ph.D.

THE  $\beta$ -iodopropionic acid required for this investigation was prepared by the direct addition of yellow phosphorus (220 grams) to a mixture of crude glyceric acid of sp. gr. 1·26 (1000 c.c.) and iodine (1700 grams). By thus modifying Beilstein's method (*Annalen*, 1861, 120, 226 ; 122, 336), the preliminary preparation of phosphorus iodide was avoided.

*Ethyl butane- $\alpha\gamma\gamma\delta\delta$ -pentacarboxylate,*

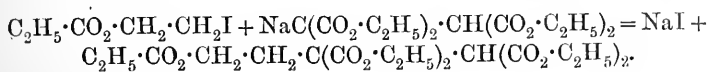


—This ester was obtained by heating together 450 grams of ethyl  $\beta$ -iodopropionate and 360 grams of dry ethyl disodioethanetetracarboxylate for 8 hours at 200°. The product after washing with water and drying with potassium carbonate, was systematically fractionated under 17 mm. pressure ; in this manner, five distinct fractions were ultimately obtained, of which the fourth was by far the largest.

This was analysed with the following result :

Found C = 54·01 ; H = 7·22.  $\text{C}_{19}\text{H}_{30}\text{O}_{10}$  requires C = 54·5 ; H = 7·2 per cent.

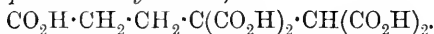
The compound, which is a colourless oil boiling at 215—218° (17 mm.), is produced in accordance with the following equation :



The formation of ethyl monosodioethanetetracarboxylate is probably due to a secondary action between ethyl  $\beta$ -iodopropionate and the disodium derivative of ethyl ethanetetracarboxylate, in which ethyl  $\Delta^{\beta\gamma}$ -dihydromuconate is produced.

The new ester is thus to be regarded as ethyl butane- $\alpha\gamma\gamma\delta\delta$ -pentacarboxylate; it readily forms sodium and haloid derivatives, the latter of which give rise to an interesting lactonic acid on treatment with silver oxide and subsequent saponification.

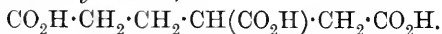
*Butane- $\alpha\gamma\gamma\delta\delta$  pentacarboxylic acid,*



—Fifty grams of ethyl butane- $\alpha\gamma\gamma\delta\delta$ -pentacarboxylate were saponified with alcoholic potash in order to isolate the corresponding pentacarboxylic acid. On acidifying with dilute nitric acid, a slight evolution of carbon dioxide occurred; the solution was accordingly neutralised and treated with silver nitrate, the precipitated silver salt of the acid was then suspended in water and decomposed with hydrogen sulphide. On evaporating the solution, a viscid syrup resulted from which no crystalline substance was obtained even after leaving the product for several weeks over sulphuric acid in a vacuum desiccator. A small quantity of the acid was therefore reconverted into the silver salt and the latter analysed.

Found  $\text{Ag} = 66.1$ .  $\text{C}_9\text{H}_5\text{O}_{10}\text{Ag}_5$  requires  $\text{Ag} = 66.4$  per cent.

*Butane- $\alpha\gamma\delta$ -tricarboxylic acid,*



—Ten grams of the pentacarboxylic acid were boiled with hydrochloric acid as long as carbon dioxide was evolved; the syrupy residue left on evaporation was then placed over sulphuric acid in a vacuum desiccator. In the course of a few days, the product solidified to a mass of prismatic needles.

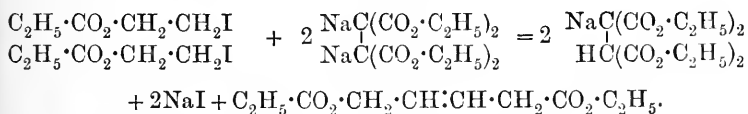
Found  $\text{C} = 44.04$ ;  $\text{H} = 5.45$ .  $\text{C}_7\text{H}_{10}\text{O}_6$  requires  $\text{C} = 44.2$ ;  $\text{H} = 5.3$  per cent.

The acid melts at  $122^\circ$  and is evidently butane- $\alpha\gamma\delta$ -tricarboxylic acid, for which the melting point is given as  $116\text{--}120^\circ$  (Auwers, Köbner, and Meyenburg, *Ber.*, 1891, 24, 2895).

*Ethyl  $\Delta^{\beta\gamma}$ -dihydromuconate,*  $\text{C}_2\text{H}_5 \cdot \text{CO}_2 \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CO}_2 \cdot \text{C}_2\text{H}_5$ .  
—Of the minor fractions, the first and third proved to be unaltered ethyl  $\beta$ -iodopropionate and ethanetetracarboxylate respectively. The second, which obstinately retained traces of iodine and boiled at  $120\text{--}125^\circ$  (17 mm.), appeared on analysis to have the formula  $\text{C}_{10}\text{H}_{16}\text{O}_4$ .

Found  $\text{C} = 59.40$ ;  $\text{H} = 7.84$ .  $\text{C}_{10}\text{H}_{16}\text{O}_4$  requires  $\text{C} = 60.0$ ;  $\text{H} = 8.0$  per cent.

From which it would appear that the compound is ethyl  $\Delta^{\beta\gamma}$ -dihydromuconate, probably produced by the condensation of two molecules of ethyl  $\beta$ -iodopropionate with loss of hydrogen iodide, on heating in the presence of ethyl disodioethanetetracarboxylate :



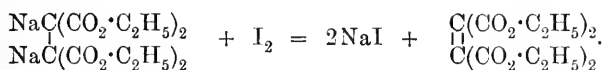
$\Delta^{\beta\gamma}$ -Dihydromuconic acid,  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CH}:\text{CH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ .—In order to establish fully the identity of the foregoing ester, 10 grams were saponified by warming with alcoholic potash. After neutralisation, the silver salt was precipitated, washed, suspended in water, decomposed with hydrogen sulphide, and the filtrate concentrated on the water-bath. From the acid purified in this manner, the silver salt was prepared and analysed.

Found  $\text{Ag} = 60.72$ .  $\text{C}_6\text{H}_6\text{O}_4\text{Ag}_2$  requires  $\text{Ag} = 60.3$  per cent.

Ethyl ethylenetetracarboxylate,  $(\text{CO}_2\cdot\text{C}_2\text{H}_5)_2\text{C}:\text{C}(\text{CO}_2\cdot\text{C}_2\text{H}_5)_2$ .—The fifth fraction of the original mixture boiled at  $227-233^\circ$  (15 mm.).

Found  $\text{C} = 53.11$ ;  $\text{H} = 6.52$ .  $\text{C}_{14}\text{H}_{20}\text{O}_8$  requires  $\text{C} = 53.2$ ;  $\text{H} = 6.3$  per cent.

The formation of this ester is probably to be traced to the interaction of ethyl disodioethanetetracarboxylate and free iodine, produced by the decomposition of ethyl  $\beta$ -iodopropionate at the high temperature of the reaction :



Ethylenetetracarboxylic Acid,  $(\text{CO}_2\text{H})_2\text{C}:\text{C}(\text{CO}_2\text{H})_2$ .—In order to establish fully the identity of the preceding ester, the acid potassium salt of this acid was prepared and analysed. To this end, 5 grams of the ester were saponified with alcoholic potash, and the solution rendered slightly acid with acetic acid; a thick, brown precipitate slowly settled, which was collected, washed with a little dilute alcohol, and dissolved in water. Absolute alcohol was then added to the solution until a slight turbidity became permanent, when the mixture was placed over quicklime in a vacuum desiccator. In the course of a few days, tiny crystals separated and were recrystallised from water and analysed.

Found  $\text{K} = 27.62$ ;  $\text{C}_6\text{H}_2\text{O}_8\text{K}_2$  requires  $\text{K} = 27.86$  per cent.

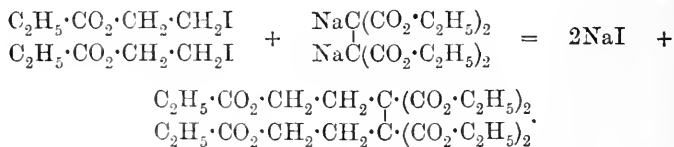
*Hexane- $\alpha\gamma\delta\zeta$ -tetracarboxylic Acid (aa-Diglutaric Acid),*  
 $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{H})\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}.$

On continuing the fractionation, the thermometer rose to  $240^\circ$  (17 mm.), when distillation practically ceased, and on raising the temperature still higher, decomposition set in. The black, tarry product still remaining in the flask was therefore subjected to the following operations, which ultimately led to the isolation of hexane- $\alpha\gamma\delta\delta\zeta$ -hexacarboxylic acid: (1) the residue saponified with alcoholic potash, diluted, neutralised, and filtered to remove neutral tarry matter; (2) the potassium salt precipitated with silver nitrate; (3) the silver salt suspended in water and decomposed with hydrogen sulphide; (4) the free acid concentrated (a) on the water-bath, and (b) in a vacuum desiccator; (5) the acid dissolved in water and saturated with calcium carbonate; (6) the calcium salt submitted to a prolonged series of fractional precipitation from aqueous solution by the addition of alcohol; (7) the least soluble fraction of calcium salt converted into silver salt by precipitation with silver nitrate; (8) the silver salt suspended in water and decomposed with hydrogen sulphide; (9) the free acid concentrated (a) on the water-bath, and (b) in a vacuum desiccator.

A small quantity of the free acid was then reconverted into the silver salt, which is an amorphous white powder obtained by adding silver nitrate to a neutral solution of the ammonium salt.

The salt appeared to be a mixture of silver hexanehexa- and tetracarboxylates. Found  $\text{Ag} = 64.04$ ;  $\text{C}_{10}\text{H}_{10}\text{O}_8\text{Ag}_4$ , requires  $\text{Ag} = 62.6$ ;  $\text{C}_{12}\text{H}_8\text{O}_{12}\text{Ag}_6$ , requires  $\text{Ag} = 65.3$  per cent.

The formation of ethyl hexane- $\alpha\gamma\delta\delta\zeta$ -hexacarboxylate is indicated as follows:



In order to convert the hexabasic acid present into the tetrabasic acid, the product was boiled with hydrochloric acid until the evolution of carbon dioxide ceased. The syrupy liquid left after evaporating the solution on the water-bath was placed in a vacuum desiccator over caustic potash to remove adhering hydrochloric acid; the residue was then dissolved in water, neutralised with ammonia, precipitated with silver nitrate, and subjected to the following treatment: (1) the silver salt suspended in water and decomposed with hydrogen sulphide; (2)

the free acid concentrated (a) on water-bath and (b) in a vacuum desiccator ; (3) the acid dissolved in water and saturated with calcium carbonate ; (4) the calcium salt fractionally precipitated by the addition of alcohol ; (5) the least soluble fraction of the calcium salt converted into silver salt by precipitation with silver nitrate ; (6) the silver salt suspended in water and decomposed with hydrogen sulphide ; (7) the free acid concentrated (a) on the water-bath and (b) in a vacuum desiccator ; (8) the free acid dissolved in water, just sufficient alcohol added to produce turbidity, and the solution placed in a vacuum desiccator over quicklime.

As the percentage of alcohol increased, owing to the absorption of the water by the quicklime, a granular, gummy solid slowly separated. The acid was then washed with dilute alcohol, dried, dissolved in anhydrous acetone, an equal volume of benzene added, and the solution allowed to remain in a vacuum desiccator over strong sulphuric acid. A gummy, semi-crystalline mass slowly separated, which, on being again subjected to this treatment, became distinctly crystalline, and after washing with ice-cold water and several crystallisations from water was obtained pure.

0.08 gave 0.13275  $\text{CO}_2$  and 0.0399  $\text{H}_2\text{O}$ . Found C = 45.26 ; H = 5.54.  
 $\text{C}_{10}\text{H}_{14}\text{O}_8$  requires C = 45.84 ; H = 5.34 per cent.

The acid crystallises in colourless prisms, sparingly soluble in organic solvents, but more readily in hot water. It melts at  $215^\circ$  with decomposition, and appears to be identical with the acid obtained by Sell and Easterfield on reducing quinhydroketopyridine (Trans., 1894, 65, 830), to which they assigned the above constitution. Unfortunately, the extremely small yield (0.108 gram) rendered further comparison impossible.

I wish to express my thanks to the Government Grant Committee of the Royal Society for a grant in aid of this investigation.

UNIVERSITY LABORATORY,  
CAMBRIDGE.

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# LXI.—*A Comparison of the Products of the Hydrolysis of Potato Starch with those obtained from Cereal Starches.*

By JAMES O'SULLIVAN.

A COMPARISON of the results obtained by Lintner's method for determining the relative diastatic power of malts (Abstr., 1887, 52, 165), with those yielded by a somewhat similar process with which I had prior experience, showed that something remained to be explained before these two series of data could be reconciled. In the latter method, potato starch paste was used, whilst in Lintner's method his soluble starch was employed. On investigating the matter, I became convinced that the products of the hydrolysis of potato starch paste by malt extract under like conditions, calculated as maltose and dextrin, were not of the same percentage composition as those yielded by Lintner's starch, the latter giving a very much higher proportion of maltose.

I have now extended this inquiry to the following starches: (1) potato starch purified by alternate treatment with large volumes of very dilute potassium hydroxide and hydrochloric acid, the product being finally washed with water until neutral; (2) malt starch and (3) barley starch I, similarly prepared; (4) barley starch II, purified, or rather prepared from the same barley as barley I by washing with water only; (5) maize starch and (6) rice starch purchased as pure; (7) Lintner's starch, prepared by Lintner's process from the above potato starch.

The water, ash, and albuminoids ( $N \times 6.25$ ) in these starches were as follows:

	Potato.	Lintner's	Malt.	Barley I.	Barley II.	Maize.	Rice.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Water .....	18.3	20.44	15.00	18.97	16.05	13.90	14.00
Ash .....	0.24	0.17	0.09	0.06	0.19	0.35	0.62
Albuminoids ...	0.17	0.09	0.30	0.23	3.42	0.23	0.45

Although it must be admitted that numbers such as these do not of themselves show the purity of starch preparations, yet, if taken in conjunction with the results obtained for them by the best method of estimating starch, devised by C. O'Sullivan (Trans., 1884, 45, 1),\* as

\* Digestion at 62—63° for one hour.

tabulated in table V, I am of opinion that with the exception of barley starch II they leave little to be desired as regards purity. If the amount of starch deduced from the maltose and dextrin, as in O'Sullivan's method, is found to be within 2 or 3 per cent. of the total quantity taken, it might be considered pure, this being apparently the only way of testing the purity of the starch preparation.

The experimental methods employed in the study of potato starch transformations are now so well known, owing to C. O'Sullivan's researches, that I need not refer to them here. It is, however, necessary to give descriptions of the preparation of the starch pastes and the preliminary treatment of the diastase and malt extract.

The amount of water in the starches employed in each series of transformations being known, the quantity of starch taken was such that the amount of dry starch in every case was the same. The quantity of dry starch is shown in column 3 of the tables.

The starch was thoroughly mixed with 25 c.c. of water, and constantly stirred, while the temperature was raised to 40°, then 50 c.c. of boiling water were added, and the beaker immersed in a steam-bath, the paste being stirred continuously with a thermometer until the temperature rose to 97°, at which temperature it was kept for 5 minutes. The beaker with its contents was placed in a bath of constant temperature, and kept covered with a watch-glass to prevent evaporation from the surface of the paste, which produces a very insoluble scum. From time to time, the pastes were stirred, and when all were at the same temperature, the hydrolytic agent was added.

The diastase "a" indicated in the tables was prepared from malt made in the usual way, and diastase "b" was obtained from a malt prepared in the laboratory and air-dried. The malt-extract was prepared from malt made in the usual way.

The quantity of diastase required for each paste in the series of transformations was carefully mixed with 10 c.c. of water in a small beaker, stirred continuously with a thermometer, and heated rapidly on a sand-bath until, in about 3—4 minutes, the required transformation temperature was reached. The diastase thus prepared was immediately added to the starch paste, the residue adhering to the small beaker being washed in as quickly as possible with water at the same temperature. The malt extract was treated in the same way as the diastase. On adding the hydrolytic agent to the paste, the mixture was quickly stirred so as to ensure a rapid and equally distributed action.

At the expiration of the time required for the digestion, the beakers containing the solutions were immersed in a steam-bath continuously stirred, and heated at 97° for 5 minutes.

The solutions, the results of which are given in tables I, II, V and VI, were cooled, and made up to 125 c.c. at  $15.5^{\circ}$ ; those of tables III and IV were concentrated and made up to 100 c.c. at  $15.5^{\circ}$ , both the solutions being then filtered through rapid filters. In each experiment, the volume of the solution undergoing hydrolysis was practically 100 c.c. The soluble solids of the diastase and malt-extract, treated as in the transformations, were determined together with their properties, and all the numbers in the tables are corrected for these. Weighed quantities of the solutions were used in determining the cupric oxide reducing power.

An allowance was made for the hydration from starch to maltose ( $\frac{\text{maltose}}{1.055} = \text{starch}$ ) in calculating the percentage of starch in column 8.

The factors employed throughout are: (1) divisor for solids in solution deduced from the density of the solution (3.95), (2) cupric oxide reducing power of maltose (K62.5), (3) dextrin ( $[\alpha]_j$  222), (4) maltose ( $[\alpha]_j$  154).

On comparing the results of the six series of transformations given in the tables, it will be seen (1) that under similar conditions of hydrolysis with diastase or malt-extract, the results obtained from potato starch show no quantitative relationship with those obtained from the other starches, potato starch differing entirely from these; (2) that the percentage composition of the products of the other starches could not be inferred from the results obtained by the hydrolysis of potato starch.

TABLE I.

*Transformation of Starches with Malt Extract (50 c.c. : 2.6 grams of Solids : Extract from about 10 grams of Malt) at 65°. Two hours' Digestion.*

1. Starch.	2. Grams.	3. Grams of dry substance.	4. Solids from solution- density in 125 c.c.	5. Composition of starch products in grams and in percentages.		6. [ $\alpha$ ] <sub>D</sub> observed for solids.	7. [ $\alpha$ ] <sub>D</sub> calculated from maltose and dextrin.	8. Percentage of starch found by	
				Maltose.	Dextrin.			O'Sullivan's method.	Solids in solution.
Potato .....	6.884	5.625	5.615	Grams. Per cent. 2.814 : 50.11	Grams. Per cent. 2.801 : 49.89	182	187	97.2	99.8
Lintner's .....	7.440 *	5.937	5.852	4.570 : 76.52	1.404 : 23.48	167	169	96.6	98.5
Malt .....	6.617	5.625	5.506	4.263 : 74.86	1.431 : 25.14	170.1	171	97.1	98.0
Barley I .....	6.941	5.625	5.501	4.231 : 76.00	1.337 : 24.00	170	170.3	95.0	98.0
Barley II .....	6.581	5.625	5.135	4.091 : 75.85	1.302 : 24.15	171.8	170.4	92.0	91.1
Maize .....	6.533	5.625	5.544	4.326 : 75.20	1.426 : 24.80	171.0	170.8	98.3	98.5
Rice .....	6.542	5.625	5.460	3.974 : 70.19	1.682 : 29.81	173.0	174.0	97.0	97.0

\* An error was detected in the calculation of moisture after this was weighed.

TABLE II.

*Transformations of Starches with Malt Extract (25 c.c. : 1.2 grams of Solids : Extract from about 5 grams of Malt) at 65°. Two hours' Digestion.*

1. Starch	2. Grams.	3 Grams of dry substance.	4. Solids from solution- density in 125 c.c.	5. Composition of starch products in grams and in percentages.		6. [ $\alpha$ ] <sub>J</sub> observed for solids.	7. [ $\alpha$ ] <sub>J</sub> calculated from maltose and dextrin.	8. Percentage of starch found by	
				Maltose.	Dextrin.			O'Sullivan's method.	Solids in solution.
Potato .....	6.126	5.000	4.971	Grams. Per cent. 2.815 : 54.10	2.387 : 45.90	188	184.1	101.0	99.5
Lintner's .....	6.150	5.000	4.831	3.814 : 75.60	1.230 : 24.40	173	171.0	98.5	96.6
Malt .....	5.881	5.000	4.353	3.648 : 72.30	1.397 : 27.70	175.7	175.7	97.1	97.0

TABLE III.

*Transformations of Starches with Diastase "a" (0.4 gram) at 60°. Eighteen hours' Digestion.*

1. Starch.	2. Grams.	3. Grams of dry substance.	4. Composition of starch products deduced from [ $\alpha$ ] <sub>J</sub> and K.		5. [ $\alpha$ ] <sub>J</sub> calculated from maltose and dextrin.	6. Percentage of starch (O'Sullivan's method).
			Maltose.	Dextrin.		
Potato .....	4.90	4.01	Grams. Per cent. 2.140 : 53.4	Grams. Per cent. 1.868 : 46.6	185.7	97.4
Lintner's .....	4.00	4.00	—	—	166.0 *	—
Malt .....	4.70	4.00	3.134 : 79.4	0.813 : 20.6	167.9	94.5

\* K was not determined in this case, and [ $\alpha$ ]<sub>J</sub> refers to solids in solution.

TABLE IV.  
*Transformations of Starches with Diastase "a" (0.2 gram) at 61°. Two hours' Digestion.*

1. Starch.	2. Grams.	3. Grams of dry substance.	4. Solids from solution- density in 100 c. c.	5. Composition of starch products in grams and in percentages.		6. [ $\alpha$ ] <sub>D</sub> obtained for solids.	7. [ $\alpha$ ] <sub>D</sub> calculated from maltose and dextrin.	8. Percentage of starch found by	
				Maltose.	Dextrin.			O'Sullivan's method.	Solids in solution.
Potato .....	4.90	4.01	3.958	Grams. Per cent. 1.021 : 26.15	Grams. Per cent. 2.882 : 73.85	204.1	204.1	96.0	98.7
Exp. I. Linthner's.	5.00	3.98	3.940	2.840 : 70.22	1.205 : 29.78	172.3	174.2	98.0	99.0
" II. "	5.00	3.98	3.948	2.771 : 68.70	1.262 : 31.30	172.6	175.1	97.7	99.1
" I. Malt .....	4.70	4.00	3.659	1.957 : 52.54	1.782 : 47.66	185.4	186.4	90.9	91.5
" II. " .....	4.70	4.00	3.669	2.220 : 59.32	1.522 : 40.67	181.0	182.0	91.9	91.9

TABLE V.  
*Transformations of Starches with Diastase "L" (0.4 gram) at 65°C. Two hours' Digestion.*

1. Starch.	2. Grams.	3. Grams of dry substance.	4. Solids from solution- density in 125 c.c.	5. Composition of starch products in grams and in percentages.		6. $[\alpha]_D$ observed for solids.	7. $[\alpha]_D$ calculated from maltose and dextrin.	8. Percentage of starch found by	
				Maltose.	Dextrin.			O'Sullivan's method.	Solids in solutions.
Potato .....	6.884	5.625	5.490	Grams. Per cent. 2.117 : 38.08	Grams. Per cent. 3.442 : 61.92	196.5	196.0	96.9	97.6
Lintner's .....	7.071	"	5.695	4.144 : 71.83	1.625 : 28.17	170.5	173.1	98.7	101.0
Malt .....	6.617	"	5.507	3.783 : 67.25	1.842 : 32.75	173.0	176.0	96.2	97.9
Barley I .....	6.941	"	5.924 *	4.182 : 66.38	2.118 : 33.62	174.5	177.1	106.0	105.0
Barley II .....	6.581	"	5.177	3.411 : 65.53	1.794 : 34.47	172.7	177.4	89.3	92.0
Maize.....	6.533	"	5.607	2.682 : 47.82	2.927 : 52.18	187.0	186.5	97.2	99.6

\* The other data indicate that, in all probability, an error was made in weighing the amount of starch.

TABLE VI.  
*Transformations of Starches with Diastase "b" (0.4 gram) at 60°. One hour's Digestion.*

1. Starch.	2. Grams.	3. Grams of dry substance.	4. Solids from solution- density in 125 c.c.	5. Composition of starch products in grams and in percentages.		6. $[\alpha]_D^{20}$ observed for solids.	7. $[\alpha]_D^{20}$ calculated from maltose and dextrin.	8. Percentage of starch found by	
				Maltose.	Dextrin.			O'Sullivan's method.	Solids in solution.
Potato .....	6.884	5.625	5.799	Grams. Per cent.	Grams. Per cent.	199.7	196.1	103	103
Lintner's .....	7.071	"	5.691	2.248 : 37.94	3.676 : 62.05	169.8	167.7	102.8	101.1
Malt .....	6.617	"	5.391	4.826 : 79.94	1.211 : 20.05	173.6	173.7	94.1	95.8
Barley I .....	6.941	"	5.425	3.896 : 70.87	1.601 : 29.13	175.7	175.5	96.9	96.4
Barley II .....	6.581	"	5.061	3.858 : 68.23	1.796 : 31.77	172.4	175.0	88.6	89.9
Maize.....	6.533	"	5.315	3.568 : 69.02	1.601 : 30.98	191.6	192.5	93.8	94.5

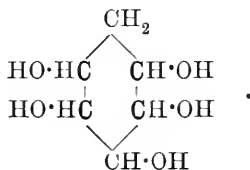
LXII.—*A Lævorotatory Modification of Quercitol.*

By FREDERICK BELDING POWER and FRANK TUTIN.

QUERCITOL has hitherto only been found in the fruits (acorns) of certain species of *Quercus*, in which it exists as a dextrorotatory modification. The lævorotatory modification now described was obtained by us from the leaves of *Gymnema sylvestre* (Br.), a plant belonging to the family of *Asclepiadaceæ*, and indigenous to Banda and the Deccan Peninsula (compare "Pharmacographia Indica," vol. II, p. 450).

In the course of an examination of a large quantity of *Gymnema* leaves, a colourless, crystalline substance having the empirical formula  $C_6H_{14}O_6$  was isolated, which melted at  $174^\circ$  and had  $[\alpha]_D -73.9^\circ$ . When heated at  $110^\circ$ , it lost one molecular proportion of water; it formed a penta-acetyl derivative,  $C_6H_7(O \cdot C_2H_3O)_5$ , and a pentabenzoyl derivative,  $C_6H_7(O \cdot C_7H_5O)_5$ . From these facts it was seen that the above formula,  $C_6H_{14}O_6$ , could be appropriately modified to  $C_6H_7(OH)_5 \cdot H_2O$ , which represents the substance as a hydrated isomeride of quercitol.

The constitutional formula of quercitol, first proposed by Kanonnikoff, represents it as pentahydroxyhexahydrobenzene,



The correctness of this formula was proved by Kiliani and Schaefer (*Ber.*, 1896, 29, 1762), who obtained malonic acid on oxidation with potassium permanganate. Moreover, the same investigators have shown that *d*-quercitol, on oxidation with aqueous bromine, forms a diketone,  $C_6H_8O_5$ , which was isolated in the form of its dihydrazone,  $C_{18}H_{20}O_3N_4$ .

The substance isolated from the leaves of *Gymnema sylvestre*, when oxidised with potassium permanganate and sodium hypobromite respectively, showed a behaviour identical with that of *d*-quercitol. Like the latter, it afforded, on the one hand, malonic acid, and, on the other, a diketotrihydroxyhexahydrobenzene, which was isolated in the form of its dihydrazone (m. p.  $209^\circ$ ).

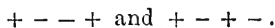
It was thus demonstrated that our substance has the same constitution as *d*-quercitol, and can only differ from the latter stereo

chemically; but, since *d*-quercitol has  $[\alpha]_D + 24.16^\circ$ , the one cannot be the optical antipode of the other.

Pentahydroxyhexahydrobenzene has four asymmetric groupings, and eight optically active modifications are therefore possible, which may be represented as follows:

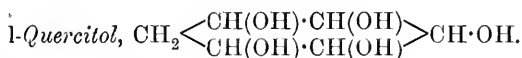


By uniting these four pairs, the corresponding racemic modifications would be obtained. The following two unresolvable inactive modifications are also possible:



Until a further number of these isomerides of quercitol are known, it will be impossible to assign a definite configuration either to *d*-quercitol or to the *l*-quercitol isolated from *Gymnema sylvestre*.

#### EXPERIMENTAL.



The leaves of *Gymnema sylvestre* were extracted with hot alcohol and the liquid concentrated to a viscid syrup. Water was then added and the greater part of the remaining alcohol removed on the water-bath. After being allowed to cool, the precipitated resins were removed by filtration. Sulphuric acid was added to the clear filtrate until no further precipitate was produced, and this precipitate, which soon agglomerated to a resinous mass, was likewise removed by filtration. The free sulphuric acid was then removed by barium hydroxide, a slight excess of basic lead acetate subsequently added to remove the colouring matter, and the combined precipitates filtered off. After depriving the filtrate of lead by means of hydrogen sulphide, it was concentrated under reduced pressure to the consistency of a viscid syrup and then diluted with alcohol, when, after a few days, the *l*-quercitol separated in a nearly pure, crystalline form, which, after being filtered at the pump, thoroughly washed with alcohol, and recrystallised from dilute alcohol, was obtained in a perfectly pure state. The amount of this substance contained in the air-dried leaves is 0.6 per cent.

*l*-Quercitol melts at  $174^\circ$ . A determination of its specific rotatory power in aqueous solution gave the following result:  $\alpha - 2^\circ 59'$ ;  $l = 1$  dcm.;  $c = 4.035$ ;  $[\alpha]_D - 73.9^\circ$ .

It is readily soluble in water, very sparingly so in alcohol, and insoluble in all other ordinary solvents. It crystallises from water in

colourless prisms containing one molecule of water, which is not lost on recrystallisation from absolute alcohol, but is eliminated when the substance is heated for some time at  $100^{\circ}$ . When crystallised from alcohol, it is obtained in the form of fine, colourless needles.

A portion of *l*-quercitol which had been recrystallised from alcohol was analysed :

0.1139 gave  $0.1650 \text{ CO}_2$  and  $0.0800 \text{ H}_2\text{O}$ .  $\text{C} = 39.5$  ;  $\text{H} = 7.8$ .

$\text{C}_6\text{H}_{12}\text{O}_5 \cdot \text{H}_2\text{O}$  requires  $\text{C} = 39.5$  ;  $\text{H} = 7.7$  per cent.

In another portion, which had been recrystallised from dilute alcohol, the water was determined by heating at  $110^{\circ}$ .

0.8963 lost  $0.0881 \text{ H}_2\text{O}$ .  $\text{H}_2\text{O} = 9.8$ .

$\text{C}_6\text{H}_{12}\text{O}_5 \cdot \text{H}_2\text{O}$  requires  $\text{H}_2\text{O} = 9.9$  per cent.

This dried substance was then recrystallised from absolute alcohol, in which it was even more sparingly soluble than the hydrated substance, and analysed :

0.1009 gave  $0.1600 \text{ CO}_2$  and  $0.0674 \text{ H}_2\text{O}$ .  $\text{C} = 43.2$  ;  $\text{H} = 7.4$ .

$\text{C}_6\text{H}_{12}\text{O}_5$  requires  $\text{C} = 43.9$  ;  $\text{H} = 7.3$  per cent.

It was therefore practically anhydrous.

*Penta-acetyl-l-quercitol*,  $\text{C}_6\text{H}_7(\text{O} \cdot \text{C}_2\text{H}_3\text{O})_5$ .

When *l*-quercitol is heated with acetic anhydride and sodium acetate, a vigorous reaction takes place before the boiling point of the anhydride is reached. After boiling for about one hour, the mixture was poured into water, when a heavy oil separated, which in a few minutes became solid. After recrystallisation from dilute alcohol, the substance was obtained in a pure state.

Penta-acetyl-*l*-quercitol crystallises in colourless needles, which melt at  $124$ — $125^{\circ}$  when anhydrous, and at  $87$ — $97^{\circ}$  when containing benzene of crystallisation. A determination of its specific rotatory power in chloroform solution gave the following result :  $\alpha = 0^{\circ}42'$  ;  $l = 1 \text{ dm.}$  ;  $c = 2.697$  ;  $[\alpha]_D - 26.0^{\circ}$ .

It is readily soluble in alcohol, ethyl acetate, acetone, benzene, ether, and chloroform, sparingly so in light petroleum, and insoluble in water. When crystallised from benzene, or a mixture of benzene and light petroleum, it contains one molecule of benzene, but from dilute alcohol it separates in an anhydrous state. The anhydrous acetyl derivative was analysed :

0.1320 gave  $0.2467 \text{ CO}_2$  and  $0.0706 \text{ H}_2\text{O}$ .  $\text{C} = 51.0$  ;  $\text{H} = 5.9$ .

0.1068 „  $0.2007 \text{ CO}_2$  „  $0.0576 \text{ H}_2\text{O}$ .  $\text{C} = 51.2$  ;  $\text{H} = 5.9$ .

$\text{C}_{16}\text{H}_{22}\text{O}_{10}$  requires  $\text{C} = 51.3$  ;  $\text{H} = 5.8$  per cent.

An attempt was made to determine the molecular weight of *l*-quercitol in phenol solution, but it was not sufficiently soluble. The acetyl derivative was therefore selected for this purpose, and its molecular weight was determined by the cryoscopic method in benzene solution.

0.4288 in 24.38 benzene gave  $\Delta t = 0.248^\circ$ . M. W. = 348.

$C_{16}H_{22}O_{10}$  requires M. W. = 374.

The number of acetyl groups in this compound was determined by hydrolysing a weighed quantity of the substance with a known volume of standard alcoholic solution of sodium hydroxide and titrating the excess of alkali with standard acid. The percentage of acetyl found by this means was 80.3, the theoretical percentage for five acetyl groups being 78.9.

It was observed that the penta-acetyl-*l*-quercitol which had been crystallised from benzene melted at  $87-97^\circ$ , but after heating to  $80^\circ$  for a short time melted at  $124-125^\circ$ , which is the melting point of the anhydrous substance. The whole of the benzene was also given off in the course of two or three days at the ordinary temperature.

A portion of the acetyl derivative was crystallised from benzene, pressed on a porous tile until free from adhering solvent, and the amount of benzene of crystallisation determined by heating at  $100^\circ$  until the weight of the residue remained constant.

0.5200 lost 0.0880  $C_6H_6$ .  $C_6H_6 = 16.9$ .

0.7142 „ 0.1239  $C_6H_6$ .  $C_6H_6 = 17.3$ .

$C_{16}H_{22}O_{10}$ ,  $C_6H_6$  requires  $C_6H_6 = 17.3$  per cent.

*Pentabenzoyl-l-quercitol*,  $C_6H_7(O \cdot C_7H_5O)_5$ .

The *l*-quercitol was benzoylated by the Schotten-Baumann method, and also by heating it with an excess of benzoyl chloride until hydrogen chloride ceased to be evolved; the products obtained were identical.

Pentabenzoyl-*l*-quercitol shows the same behaviour towards solvents as the acetyl derivative; it separates from alcohol in an amorphous state, melts at  $133^\circ$ , and is anhydrous. A determination of its specific rotatory power in chloroform solution gave the following result:  $\alpha = 2.14'$ ;  $l = 1$  dm.;  $c = 2.826$ ;  $[\alpha]_D = 79.0^\circ$ .

On adding a quantity of light petroleum to a solution of the substance in a mixture of warm ethyl acetate and alcohol, needle-shaped crystals containing one molecule of alcohol slowly separated. These crystals, when dried in the air, melt at  $116^\circ$ , but the melting point is raised to

148° after drying at 100° for some hours. The amount of alcohol of crystallisation was estimated by heating at 120°.

0.7703 lost 0.0503  $C_2H_6O$ .  $C_2H_6O = 6.5$ .

$C_{41}H_{32}O_{10}$ ,  $C_2H_6O$  requires  $C_2H_6O = 6.3$  per cent.

The dried substance was then analysed :

0.1000 gave 0.2630  $CO_2$  and 0.0436  $H_2O$ .  $C = 71.7$  ;  $H = 4.8$ .

$C_{41}H_{32}O_{10}$  requires  $C = 71.9$  ;  $H = 4.7$  per cent.

*l*-Quercitol readily forms a phenylurethane, but this derivative crystallises with difficulty, and we were unable to obtain it in a pure state ; it melts indefinitely between 245° and 260°.

*Oxidation with Sodium Hypobromite. Formation of a Diketotrihydroxyhexahydrobenzene*,  $C_6H_5O_2(OH)_3$ .

By the oxidation of *d*-quercitol with bromine in the presence of water, Kiliani obtained a diketone which he isolated in the form of its dihydrazone, but did not obtain this in a state of purity (*Ber.*, 1896, 29, 1762). In the case of *l*-quercitol, we have found that its oxidation can be effected much more quickly and more satisfactorily by the use of sodium hypobromite.

Twenty grams of *l*-quercitol and 90 grams of crystallised sodium carbonate were dissolved in water (about 400 c.c.) and the mixture cooled in ice. Thirty-five grams of bromine were then gradually added, and the mixture allowed to remain at the ordinary temperature for about 2 hours, when the colour of the bromine had disappeared. A slight excess of sulphuric acid was then added, and the liberated bromine removed by means of sulphur dioxide. The liquid, after being made slightly alkaline with potassium hydroxide, was acidified with acetic acid. Thirty grams of phenylhydrazine, dissolved in 30 grams of 50 per cent. acetic acid, were then added, and in the course of two days the mixture deposited a large quantity of dark red, tarry matter, mixed with minute needles of the dihydrazone. This sticky mass was collected at the pump, and the red, tarry matter removed by washing with ethyl acetate. A bright yellow, crystalline substance remained on the filter, which, after crystallisation from alcohol, in which it was somewhat sparingly soluble, melted with decomposition at 209°.

0.0963 gave 0.2233  $CO_2$  and 0.0519  $H_2O$ .  $C = 63.2$  ;  $H = 5.9$ .

0.1046 „ 0.2424  $CO_2$  „ 0.0566  $H_2O$ .  $C = 63.2$  ;  $H = 6.0$ .

0.1334 „ 19.8 c.c. moist nitrogen at 23° and 770 mm.  $N = 16.9$ .

$C_{18}H_{20}O_3N_4$  requires  $C = 63.5$  ;  $H = 5.9$  ;  $N = 16.5$  per cent.

*Oxidation with Potassium Permanganate. Formation of Malonic Acid.*

A cold, dilute, aqueous potassium permanganate solution was gradually added to a cold, dilute, aqueous solution of *l*-quercitol. The colour of the permanganate was only very slowly discharged at first, but after a few portions had been introduced, the reaction proceeded much more quickly. When the equivalent of nearly eight atoms of oxygen had been added, the colour of the permanganate ceased to be discharged. The precipitated manganese dioxide was then removed and the oxalic and carbonic acids subsequently precipitated by the addition of an excess of calcium chloride. The filtrate was then evaporated to dryness, the powdered residue mixed with absolute alcohol, and the mixture boiled in a reflux apparatus for six hours, while dry hydrogen chloride was simultaneously passed through it. After distilling off the greater part of the alcohol, water was added, when the characteristic odour of ethyl malonate was perceptible. This liquid was then extracted with ether, and, after removing the latter, the residue was distilled, first under reduced, and finally under the ordinary pressure. A fraction boiling at 197—202° was analysed.

0.1175 gave 0.2256 CO<sub>2</sub> and 0.0804 H<sub>2</sub>O. C = 52.3; H = 7.6.

C<sub>7</sub>H<sub>12</sub>O<sub>4</sub> requires C = 52.5; H = 7.5 per cent.

Kiliani (*loc. cit.*) identified the malonic acid formed by the oxidation of *d*-quercitol by analyses of its barium and calcium salts.

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LXIII.—*The Constituents of the Essential Oil of Californian Laurel.*

By FREDERICK BELDING POWER and FREDERIC HERBERT LEES.

THE Californian laurel, *Umbellularia Californica* (Nuttall), is a handsome, evergreen tree, which is distributed from the valleys of Oregon through the California coast ranges and along the high western slopes of the Sierra Nevada to the southern slopes of the San Bernardino Mountains (compare "The Silva of North America," by Charles Sprague Sargent, vol. vii, pp. 19—22, tab. cccvi.). It is also known under the names of "mountain laurel," "cajeput," "spice tree," "California olive," "California bay-tree," and "pepper-wood."\*

\* The name of "pepper-wood" has also been given to a species of *Xanthoxylum*.

The essential oil, which is distilled from the leaves,\* has been described as having a pale yellow colour, and a pungent, aromatic odour, resembling that of a mixture of nutmeg and cardamom. When inhaled in any considerable amount, it attacks the mucous membranes, produces headache, and excites a flow of tears ("Die aetherischen Oele," by Gildemeister and Hoffmann, p. 527).

The only chemical examination hitherto made of this oil which requires notice is that by Stillman (*Ber.*, 1880, 13, 629, and *Amer. Chem. J.*, 1880, 2, 38), who obtained by its fractional distillation two principal fractions, boiling respectively at 167—168° and 215—216°. The fraction 167—168° was regarded by Stillman as having the formula  $C_{20}H_{32}.H_2O$ , and as corresponding with the "terpinol" of Wiggers, which, however, has since been shown to be a mixture of several substances. To the fraction 215—216°, which he observed to possess the pungency characteristic of the original oil, was assigned the formula  $C_8H_{12}O$  and the name of "umbellol," but without any determination of its chemical nature. From the results of our investigation, it is evident that both of the fractions analysed by Stillman consisted of a mixture of substances.

#### EXPERIMENTAL.

The oil employed in this investigation (1200 grams), which was specially distilled for us in California, and was therefore perfectly genuine, had a pale yellow colour, and an odour which at first was agreeably aromatic and somewhat camphoraceous, but, as has previously been noticed, when strongly inhaled it is exceedingly pungent, affecting particularly the mucous membranes of the nose and eyes. Its sp. gr. was 0.9483 at 16°/16°, and its optical rotatory power - 22° in a 100 mm. tube. The oil was completely soluble in 1.5 parts of 70 per cent. alcohol; it formed no solid compound with sodium hydrogen sulphite. As it was thought that it might contain sulphur or nitrogen compounds, special tests were made for these elements, but with negative results.

A determination of the amount of free acids and of esters gave the following data: 10.35 grams of the oil required 1.5 c.c. of a seminormal alcoholic solution of sodium hydroxide to neutralise the free acids. On subsequently adding an excess of the alkali solution and boiling, it was found that only 0.8 c.c. was required to hydrolyse the esters present. These, if calculated as  $C_{10}H_{17}.C_2H_3O_2$ , would therefore only amount to 0.8 per cent. It was observed that, on boiling the oil with

\* Schimmel & Co., in the appendix to their *Bericht* for October, 1887, p. 47, have recorded a yield of 7.6 per cent. of essential oil from the leaves of Californian laurel, and others have noted yields varying between 2.5 and 4 per cent.

an excess of an alcoholic solution of sodium hydroxide, its pungent odour was not destroyed.

The separation of the small amount of uncombined acids was effected by shaking the oil four times with dilute aqueous sodium carbonate and finally with water. The combined aqueous liquids, after shaking with ether to remove adhering oil, were evaporated to a small volume, acidified with sulphuric acid, and distilled in steam. From the distillate, ether extracted 2·3 grams of a light yellow, somewhat pungent, oily acid, which was converted through the ammonium salt into a silver salt. The latter formed a dense, white, amorphous precipitate, and was obtained in two fractions, which were analysed :

(a) 0·1523 gave 0·0495 Ag.  $\text{Ag} = 32\cdot5$ .

(b) 0·1277 „ 0·0599 Ag.  $\text{Ag} = 46\cdot9$  per cent.

The aqueous liquid from which the oily acids had been extracted still contained an acid, which was converted into its barium salt. This was crystalline, but, in attempting to prepare the corresponding silver salt, the dense, white precipitate first produced almost immediately became reduced. Another portion of the barium salt gave a precipitate of calomel with a solution of mercuric chloride. The oil thus evidently contains an exceedingly small amount of formic acid, associated with a mixture of some higher fatty acids.

#### *Identification of Eugenol.*

The whole of the oil, after the removal of the fatty acids, was shaken six times with 5 per cent. aqueous potassium hydroxide, and finally several times with water. The combined alkaline liquids were then shaken with ether to remove adhering oil, and acidified with sulphuric acid, when a quantity of an oily liquid separated ; this was taken up with ether, the ethereal solution washed, dried, and the ether removed. The residual oil, amounting to 20 grams, was then distilled under 80 mm. pressure, when it passed over completely between  $170^{\circ}$  and  $175^{\circ}$ , but principally at  $170$ — $172^{\circ}$ . A fraction collected at the latter point was analysed :

0·1106 gave 0·2964  $\text{CO}_2$  and 0·0749  $\text{H}_2\text{O}$ .  $\text{C} = 73\cdot1$  ;  $\text{H} = 7\cdot5$ .

$\text{C}_{10}\text{H}_{12}\text{O}_2$  requires  $\text{C} = 73\cdot2$  ;  $\text{H} = 7\cdot3$  per cent.

It gave a blue coloration with ferric chloride, and afforded a benzoyl derivative, which, after crystallisation from alcohol, melted at  $69$ — $70^{\circ}$ . It is thus shown that the oil contains an appreciable amount of eugenol.

*Fractional Distillation of the Oil.*

The whole of the oil remaining from the foregoing treatment was mixed with a quantity of ether and dried with calcium chloride. After the removal of the ether, the residual oil was first distilled under the ordinary pressure until the temperature had reached  $207^{\circ}$ , and then under diminished pressure. In this way, a small amount of dark, non-volatile matter was removed. The whole of the distilled oil was then subjected to a prolonged series of fractional distillations under the ordinary pressure, when a number of fractions were obtained boiling between the following ranges of temperature:  $150-165^{\circ}$ ;  $165-169^{\circ}$ ;  $169-173^{\circ}$ ;  $173-175^{\circ}$ ;  $175-180^{\circ}$ ;  $180-185^{\circ}$ ;  $185-195^{\circ}$ ;  $195-205^{\circ}$ ;  $205-215^{\circ}$ ;  $215-217^{\circ}$ ;  $217-222^{\circ}$ ;  $222-227^{\circ}$ ;  $227-235^{\circ}$ ;  $235-245^{\circ}$ ;  $245-250^{\circ}$ .

*Identification of Pinene.*

*Fraction*  $150-165^{\circ}$  (sp. gr. =  $0.8659$  at  $16^{\circ}/16^{\circ}$ ;  $\alpha_D - 20^{\circ}$  in a 100 mm. tube).—This was a colourless, limpid liquid, having a terpene-like odour, and was practically insoluble in 70 per cent. alcohol.

$0.1491$  gave  $0.4672$   $\text{CO}_2$  and  $0.1567$   $\text{H}_2\text{O}$ .  $\text{C} = 85.5$ ;  $\text{H} = 11.7$ .

$\text{C}_{10}\text{H}_{16}$  requires  $\text{C} = 88.2$ ;  $\text{H} = 11.8$  per cent.

This fraction, which evidently consisted chiefly of a hydrocarbon, associated with a small amount of an oxygenated substance which could not be eliminated by fractional distillation, was shown to contain *l*-pinene by the formation of a crystalline nitrosocbchloride, from which were prepared the nitrolpiperidine and nitrolbenzylamine, melting respectively at  $119-120^{\circ}$  and  $124-125^{\circ}$ .

*Fraction*  $165-169^{\circ}$  (sp. gr. =  $0.8770$  at  $16^{\circ}/16^{\circ}$ ;  $\alpha_D - 18^{\circ}20'$  in a 100 mm. tube).—This fraction had an odour recalling that of pinene, but was also somewhat camphoraceous; it consisted principally of pinene, but contained more of the oxygenated substance than the preceding fraction.

*Fraction*  $169-173^{\circ}$  (sp. gr. =  $0.8903$  at  $16^{\circ}/16^{\circ}$ ;  $\alpha_D - 13^{\circ}12'$  in a 100 mm. tube).—This fraction had a more highly camphoraceous odour than the preceding fraction; it was specially tested for phellandrene, but with a negative result.

*Fraction*  $173-175^{\circ}$ .—This was relatively small in amount.

*Identification of Cineol.*

*Fraction* 175—180° (sp. gr. = 0.9092 at 16°/16°;  $n_D - 3^{\circ}30'$  in a 100 mm. tube).—This very large fraction was a colourless liquid, possessing the characteristic, camphoraceous odour of cineol.

0.1144 gave 0.3381 CO<sub>2</sub> and 0.1205 H<sub>2</sub>O. C = 80.6; H = 11.7.

C<sub>10</sub>H<sub>18</sub>O requires C = 77.9; H = 11.7 per cent.

This fraction evidently consisted principally of an oxygenated substance, associated with only a small proportion of a hydrocarbon. With tetraiodopyrrole it afforded the crystalline, double compound of cineol, C<sub>10</sub>H<sub>18</sub>O, C<sub>4</sub>I<sub>4</sub>NH, which melted at 115° with decomposition (Hirschsohn, *Pharm. Zeit. Russ.*, 1893, 32, 49, 67). Cineol hydrobromide was accordingly prepared by saturating a cooled solution of the fraction in light petroleum with hydrogen bromide, and then decomposed with sodium carbonate, when the regenerated cineol\* was recognised by its physical properties and by analysis:

0.1293 gave 0.3672 CO<sub>2</sub> and 0.1368 H<sub>2</sub>O. C = 77.5; H = 11.8.

C<sub>10</sub>H<sub>18</sub>O requires C = 77.9; H = 11.7 per cent.

Sp. gr. = 0.9276 at 16°/15°. Optically inactive.

Limonene and dipentene were also sought for in this fraction by attempting to form their respective crystalline tetrabromides, but only an oily bromo-compound resulted, which did not become crystalline even after several days.

*Fractions* 180—185° and 185—195°.—These two fractions were relatively very small in amount. They had a pronounced odour of cineol, and evidently consisted of that substance together with a small amount of the constituents of the fractions of higher boiling point.

*Fraction* 195—205° (sp. gr. = 0.9308 at 15°/15°;  $n_D - 22^{\circ}48'$  in a 100 mm. tube).—This was a very small fraction.

0.1036 gave 0.3015 CO<sub>2</sub> and 0.1012 H<sub>2</sub>O. C = 79.4; H = 10.9.

0.1020 „ 0.2978 CO<sub>2</sub> and 0.0990 H<sub>2</sub>O. C = 79.6; H = 10.8 per cent.

It had the odour of the preceding fractions containing cineol and also the peculiar pungency of a fraction of higher boiling point. It was specially tested for linalool by the oxidation of 5 grams of the liquid

\* The presence of cineol in this oil appears to have first been observed by Schimmel & Co., since, in the appendix to their *Bericht* of October, 1893, p. 27, and also of April, 1897, p. 31, it is recorded as the only known constituent of the oil. This has been overlooked in the notice of the oil given in “*Die aetherischen Oele*,” by Gildemeister and Hoffmann, p. 527.

with chromic acid, but no evidence of the formation of citral was obtained.

*Fraction 205—215°* (sp. gr. = 0.9460 at 15°/15°;  $\alpha_D - 30.3'$  in a 100 mm. tube).—This fraction, which was comparatively small, had a very pungent odour, and did not differ very essentially from the large, principal fraction collected at 217—222°.

0.1036 gave 0.3011 CO<sub>2</sub> and 0.0944 H<sub>2</sub>O. C = 79.2; H = 10.1.

0.0870 „ 0.2510 CO<sub>2</sub> „ 0.0810 H<sub>2</sub>O. C = 78.7; H = 10.3 per cent.

Although these results indicated that this fraction consisted principally of the constituent of the large fraction boiling at 217—222°, the possibility of the presence of a small amount of camphor or of borneol was not precluded. In order to test for these two substances, 10 grams of the liquid were oxidised by warming for half an hour on a water-bath, with occasional vigorous shaking, with a solution of 80 grams of potassium dichromate and 120 grams of sulphuric acid in 200 c.c. of water. During the oxidation, the odour of camphor did not become apparent, and on subsequently diluting the mixture with water and distilling in steam no camphor was found in the distillate.

*Fraction 215—217°* (sp. gr. = 0.9546 at 15.5°/15°;  $\alpha_D - 34.35'$  in a 100 mm. tube).—These and other characters afforded evidence that this consisted to a very large extent of the constituent of the following fraction.

#### *Isolation of a New Ketone, Umbellulone, C<sub>10</sub>H<sub>14</sub>O.*

*Fraction 217—222°* (sp. gr. = 0.9614 at 15.5°/15°;  $\alpha_D - 36.33'$  in a 100 mm. tube).—This fraction, which was the largest obtained and contained the most interesting constituent of the oil, was colourless, had a somewhat mint-like odour, and possessed in a high degree the peculiar pungency characteristic of the original oil.

0.1144 gave 0.3309 CO<sub>2</sub> and 0.1014 H<sub>2</sub>O. C = 78.9; H = 9.9 per cent.

During the distillation of this large fraction, it was observed that the most constant boiling point was 218° (752 mm.). A quantity collected at this point was also analysed, and the physical constants determined:

0.1226 gave 0.3566 CO<sub>2</sub> and 0.1078 H<sub>2</sub>O. C = 79.3; H = 9.8.

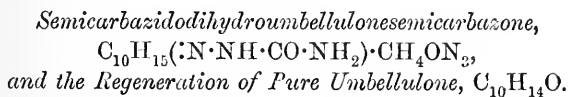
0.0958 „ 0.2780 CO<sub>2</sub> „ 0.0847 H<sub>2</sub>O. C = 79.1; H = 9.8 per cent.

Sp. gr. = 0.9584 at 15°/15°;  $\alpha_D - 37'$  in a 100 mm. tube.

From these data, and from a consideration of the analytical figures and physical constants of the smaller fractions boiling below the fraction 217—222°, it seemed evident that this consisted mainly of a substance

having the formula  $C_{10}H_{14}O$ , which requires  $C=80.0$ ;  $H=9.3$  per cent. The substance readily interacted with semicarbazide and hydroxylamine respectively, but did not respond to Schiff's rosaniline test for aldehydes; it is, therefore, a ketone. Among all the ketones which have hitherto been isolated from essential oils, none has the peculiar and extreme pungency of this substance, and there is only one of the naturally occurring ketones, namely, carvone, with which it is isomeric. Furthermore, a study of its behaviour towards many reagents has shown that it is not identical with any of the ketones hitherto described. We have, therefore, in consideration of its botanical source, given it the designation of *umbellulone*.

Umbellulone does not combine with sodium hydrogen sulphite, nor does it, like its isomeride, carvone, form a compound with hydrogen sulphide. It combines directly with two atomic proportions of bromine in the cold, and readily decolorises a cold solution of potassium permanganate. It, therefore, would seem to contain only one ethylenic linking, and, since it has the formula  $C_{10}H_{14}O$ , would appear to be a cyclic ketone with two closed rings. Its behaviour towards semicarbazide and hydroxylamine is abnormal, inasmuch as under the usual conditions these bases not only interact with the carbonyl group with the elimination of water to form a semicarbazone and oxime respectively, but at the same time their elements become attached to the two carbon atoms of the ethylenic linking. This behaviour of certain unsaturated open chain and closed ring ketones has previously been observed by Harries and his pupils (*Ber.*, 1897, 30, 230), by Tiemann (*Ber.*, 1897, 30, 251, and 1900, 33, 562), and more recently, with regard to the action of semicarbazide, by Rupe and Schlochoff (*Ber.*, 1903, 36, 4377).



To a solution in the minimum amount of water of a large excess of semicarbazide hydrochloride (40 grams) and sodium acetate (50 grams) were added umbellulone (20 grams) and just sufficient methyl alcohol to form a clear solution. After three days, during which interval nothing separated, a quantity of water was added, which caused the deposition of a bulky, white, crystalline substance. This was collected and drained at the pump, and then washed well with water in order to remove the uncombined ketone, since it was found that after the first two days the reaction proceeds very slowly, and the yield of product therefore never greatly exceeded 50 per cent. of the calculated amount. As thus obtained, the compound melted at  $216^\circ$  with

evolution of gas, and was practically pure. It was recrystallised from ethyl alcohol, when it separated almost completely from the cooled solution in compact rosettes of fine needles, which melted at  $217^{\circ}$  with evolution of gas.

0.1751 gave 0.3276  $\text{CO}_2$  and 0.1260  $\text{H}_2\text{O}$ .  $\text{C} = 51.0$ ;  $\text{H} = 8.0$ .

0.1222 „ 0.2288  $\text{CO}_2$  „ 0.0885  $\text{H}_2\text{O}$ .  $\text{C} = 51.1$ ;  $\text{H} = 8.0$  percent.

It is readily soluble in hot water, without decomposition, and on cooling it separates in small, transparent, cubical crystals, which melt at  $217^{\circ}$  with evolution of gas.

0.1128 gave 0.2120  $\text{CO}_2$  and 0.0810  $\text{H}_2\text{O}$ .  $\text{C} = 51.2$ ;  $\text{H} = 8.0$ .

0.1268 „ 32.2 c.c. moist nitrogen at  $22^{\circ}$  and 766 mm.  $\text{N} = 29.0$ .

$\text{C}_{12}\text{H}_{22}\text{O}_2\text{N}_6$  requires  $\text{C} = 51.1$ ;  $\text{H} = 7.8$ ;  $\text{N} = 29.8$  per cent.

Semicarbazidodihydroumbellulonesemicarbazone is soluble in dilute mineral acids, and, on warming the solutions, it is decomposed, regenerating umbellulone in quantitative yield. This process has been utilised in order to prepare a pure specimen of the ketone for the determination of its physical constants.

A quantity of the semicarbazidosemicarbazone, mixed with about 500 c.c. of water and sufficient sulphuric acid added to effect decomposition, was distilled in steam; the umbellulone contained in the distillate was extracted with ether, the ethereal solution dried with calcium chloride, and the ether removed. The residual liquid was then distilled, when it was found to boil at  $219\text{--}220^{\circ}$  (corr.) under 749 mm. pressure. It is a perfectly colourless liquid, the odour of which is at first pleasant, somewhat resembling that of mint, but when more strongly inhaled is exceedingly pungent, producing the effects already described.

0.1634 gave 0.4778  $\text{CO}_2$  and 0.1370  $\text{H}_2\text{O}$ .  $\text{C} = 79.7$ ;  $\text{H} = 9.3$ .

0.1400 „ 0.4083  $\text{CO}_2$  „ 0.1195  $\text{H}_2\text{O}$ .  $\text{C} = 79.5$ ;  $\text{H} = 9.5$ .

$\text{C}_{10}\text{H}_{14}\text{O}$  requires  $\text{C} = 80.0$ ;  $\text{H} = 9.3$  per cent.

Sp. gr. = 0.9581 at  $15^{\circ}/15^{\circ}$ ;  $[\alpha]_{\text{D}} - 37^{\circ}$ .

*Hydroxylaminodihydroumbelluloneoxime*,  $\text{C}_{10}\text{H}_{15}(\text{N}\cdot\text{OH})\cdot\text{NH}\cdot\text{OH}$ .

Umbellulone (15 grams) was added to a solution of hydroxylamine (four molecular proportions), formed by adding a solution of sodium methoxide in methyl alcohol (9.2 grams Na in 300 c.c. methyl alcohol) to a solution of hydroxylamine hydrochloride (28 grams) in the same solvent (300 c.c.). The mixture was then boiled for two hours. After removing the methyl alcohol completely by distillation, the residue, consisting of the product of the reaction mixed with sodium

chloride, was mixed with water and the undissolved viscid oil extracted with ether, the ethereal liquid being then washed, dried, and distilled to remove the solvent. The product, which weighed 18 grams, was a clear, nearly colourless liquid of a honey-like consistency.

In order to remove a small amount of substance which had not been converted into oxime, the product was mixed with dilute sulphuric acid, in which the hydroxylamino-oxime is readily soluble, and the small amount of non-basic matter which remained as an oil was then removed by extraction with ether. By the addition of sodium carbonate to the acid aqueous liquid, the base was again set free; it was then extracted with ether, dried, and the ether removed by distillation on the water-bath and by subsequently exposing the substance in a vacuum-desiccator over paraffin wax. The base was thus obtained as a hard, slightly green, glistening, amorphous substance, which could readily be powdered; it has thus far not been possible to obtain it in a definite crystalline form.

0.2035 gave 23.2 c.c. moist nitrogen at 23° and 768 mm.  $N = 13.0$ .

$C_{10}H_{18}O_2N_2$  requires  $N = 14.1$  per cent.

Although the percentage of nitrogen obtained is somewhat less than that required by theory for the pure substance, the result is sufficiently conclusive to show its composition, inasmuch as the normal oxime,  $C_{10}H_{14}N \cdot OH$ , would require  $N = 8.5$  per cent. The discrepancy is in all probability due to the product containing a small amount of hydroxylaminodihydroumbellulone,  $C_{10}H_{15}O \cdot NH \cdot OH$ , which would not only be more readily formed than the normal oxime, but would be markedly basic, and therefore more likely to be present than the latter, which, on account of its feebly basic properties, would be readily removed by ether from a solution of the product in dilute acids (compare Harries, *loc. cit.*, and Tiemann, *loc. cit.*).

Hydroxylaminodihydroumbelluloneoxime very closely resembles diacetonehydroxylamine (*Ber.*, 1898, 31, 1376), hydroxylaminodihydropulegone (pulegonehydroxylamine, *ibid.*, 1809), and hydroxylaminodihydrocarvoxime (oxaminocarvoxime, *ibid.*, 1810). It is readily soluble in dilute alkali hydroxides and also in dilute acids, forming salts. Its solution in aqueous sodium hydroxide reduces Fehling's solution with extraordinary readiness, even in the cold.

Fraction 222—227° (sp. gr. = 0.9842 at 15°/15°;  $\alpha_D - 29.17'$  in a 100 mm. tube).—This was a comparatively small fraction, which had a pronounced odour of umbellulone and a faint one of safrole; it consisted chiefly of umbellulone, with smaller amounts of the constituents of the following fractions.

*Identification of Safrole.*

*Fraction 227—235°* (sp. gr. = 0.9976 at 15°/15°;  $\alpha_D - 20^\circ 27'$  in a 100 mm. tube) —This fraction, which was somewhat larger than the preceding one, was slightly pungent, but at the same time possessed the unmistakable odour of safrole.

While distilling this fraction it was observed that it boiled most constantly at 230—231°. A small amount was therefore separately collected at this point for analysis and the determination of its physical constants:

0.0851 gave 0.2411 CO<sub>2</sub> and 0.0680 H<sub>2</sub>O. C = 77.3; H = 8.9 per cent.

Sp. gr. = 0.9930 at 16°/16°;  $\alpha_D - 25^\circ 4'$  in a 100 mm. tube.

In order to confirm the above indication of the presence of safrole, and at the same time to ascertain whether geraniol was present, 10 grams of the liquid were oxidised by warming gently on a water-bath, with occasional shaking, with a solution of 50 grams of potassium dichromate and 16 grams of sulphuric acid in 160 c.c. of water. The brown oily product, when isolated by extraction with ether, had the odour of piperonal, but not of citral; it was vigorously shaken with a saturated solution of sodium hydrogen sulphite, when, after some time, a crystalline compound separated, which was collected, washed with ether, and decomposed with a dilute solution of sodium hydroxide. The small amount of liberated oil which was extracted with light petroleum became crystalline on introducing a trace of piperonal. The crystals melted at 35°, and had the characteristic odour of piperonal. It was thus shown that the essential oil contains safrole, but only in very small amount.

*Fraction 235—245°* (sp. gr. = 1.013 at 15°/15°;  $\alpha_D - 8^\circ 40'$  in a 100 mm. tube).—This fraction was equal in amount to the preceding, and it had the odour of safrole. During its distillation, a small amount was separately collected at 240°, when the temperature was most constant. This was analysed and its physical constants determined:

0.0846 gave 0.2361 CO<sub>2</sub> and 0.0664 H<sub>2</sub>O. C = 76.1; H = 8.7 per cent.

Sp. gr. = 1.009 at 16°/16°;  $\alpha_D - 11^\circ 41'$  in a 100 mm. tube.

This fraction consisted to a large extent of the constituent of the following fraction.

*Identification of Eugenol Methyl Ether.*

*Fraction 245—250°* (sp. gr. = 1.021 at 16°/16°;  $\alpha_D - 2^\circ 22'$  in a 100 mm. tube).—This was a large fraction, which had a slightly yellow

colour and was nearly odourless. The greater portion was observed to boil at 248—250°, and a quantity was therefore separately collected at this point for the purpose of analysis and the determination of its physical constants:

0.1035 gave 0.2846 CO<sub>2</sub> and 0.0796 H<sub>2</sub>O. C = 75.0; H = 8.5.

C<sub>11</sub>H<sub>14</sub>O<sub>2</sub> requires C = 74.2; H = 7.9 per cent.

This fraction was shown to consist of eugenol methyl ether by the fact that it readily afforded an excellent yield of bromoeugenol methyl ether dibromide, C<sub>6</sub>H<sub>2</sub>Br(O·CH<sub>3</sub>)·C<sub>3</sub>H<sub>5</sub>Br<sub>2</sub>, which, after crystallisation from ethyl alcohol, melted at 78—79° (compare Power and Lees, *Trans.*, 1902, 81, 68). Furthermore, on oxidation with potassium permanganate, it yielded veratric acid, melting at 177°.

### *Summary.*

The results of this investigation have shown that the essential oil of Californian laurel contains the following substances:

	Approximate percentage amount.
1. Eugenol ... ..	1.7
2. <i>l</i> -Pinene ... ..	6.0
3. Cineol ... ..	20.0
4. <i>Umbellulone</i> , C <sub>10</sub> H <sub>14</sub> O ... ..	60.0
5. Safrole ... ..	A very small amount.
6. Eugenol methyl ether ... ..	10.0
7. A mixture of fatty acids containing formic acid ... ..	A very small amount.

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## LXIV.—*Some Derivatives of Umbellulone.*

By FREDERIC HERBERT LEES.

IN the preceding paper, it was shown that the new unsaturated ketone, umbellulone, C<sub>10</sub>H<sub>14</sub>O, as compared with the majority of ketones, behaves abnormally in its interactions with hydroxylamine and with semicarbazide, for not only does its carbonyl group undergo the usual transformation by reacting with one molecule of the respective

base, but, in each case, the elements of a second molecule of the latter become attached to the molecule of the ketone. The products, therefore, represent the interaction of one molecule of umbellulone with two molecules of hydroxylamine or semicarbazide.

A behaviour of this kind in respect to the interaction of hydroxylamine or semicarbazide with certain unsaturated ketones has been previously observed in many instances, particularly by Harries and his pupils (*Ber.*, 1899, 32, 1317), by Tiemann, and quite recently with regard to the action of semicarbazide, by Rupe and Schlochoff (compare this vol., p. 635).

It has been shown by these authors that the abnormal behaviour under consideration is common to those ketones which contain an ethylenic linking in an  $\alpha\beta$ -position with respect to the carbonyl group.

In the hope of ultimately elucidating the constitution of umbellulone, its behaviour towards a number of reagents is being studied, and some of the results obtained are recorded in this paper.

Umbellulone combines directly, in the cold, with only two atomic proportions of bromine, forming *umbellulone dibromide*,  $C_{10}H_{14}OBr_2$ ; it would therefore seem to contain only one ethylenic linking. From its formula,  $C_{10}H_{14}O$ , and the foregoing considerations, umbellulone would appear to be an  $\alpha\beta$ -unsaturated cyclic ketone, containing two closed rings.

When umbellulone dibromide is slowly heated under diminished pressure, it rapidly becomes decomposed with evolution of hydrogen bromide. The product of this decomposition is an *unsaturated bromoketone*, having the formula  $C_{10}H_{13}OBr$  (b. p. 140—145°/20 mm.); but, besides this, *dibromodihydroumbellulone*,  $C_{10}H_{14}OBr_2$  (m. p. 119—119.5°) is also formed, the latter being probably the result of the subsequent combination of the unsaturated bromoketone with the elements of hydrogen bromide.

The unsaturated bromoketone,  $C_{10}H_{13}OBr$ , on reduction with zinc dust and acetic acid, becomes converted into a *saturated ketone*,  $C_{10}H_{16}O$  (b. p. 214—217°).

When dibromodihydroumbellulone is reduced with zinc dust and acetic acid, it is only found possible to eliminate one bromine atom with the formation of *bromodihydroumbellulone*,  $C_{10}H_{15}OBr$  (m. p. 58—59°). When the latter, however, is reduced by means of sodium and alcohol, *tetrahydroumbellulol*,  $C_{10}H_{19}OH$ , is produced (b. p. 207—208°/760 mm.).

Both dibromodihydroumbellulone and bromodihydroumbellulone behave as saturated substances, since they do not decolorise a solution of bromine in chloroform, even on boiling. In view of this fact, the formation of tetrahydroumbellulol,  $C_{10}H_{20}O$ , from bromodihydro-

umbellulone,  $C_{10}H_{15}OBr$ , can only be explained on the assumption that one of the two closed rings present in umbellulone, dibromodihydroumbellulone, and bromodihydroumbellulone becomes resolved by reduction in passing to the alcohol.

Umbellulone is readily oxidised by cold permanganate, yielding a lactone,  $C_9H_{12}O_2$  (b. p.  $217-221^\circ$ ), together with several acids which, on account of insufficiency of material, have not yet been investigated.

#### EXPERIMENTAL.

##### *Action of Bromine on Umbellulone. Formation of Umbellulone Dibromide, $C_{10}H_{14}OBr_2$ .*

Twenty grams of umbellulone were dissolved in 100 c.c. of dry chloroform, and the solution cooled in a freezing mixture. A solution of 25 grams of dry bromine in 100 c.c. of dry chloroform was then run in, drop by drop; the bromine was instantaneously absorbed, and without any evolution of hydrogen bromide. When all the bromine had been added, the colour of the solution was red, and on this remaining permanent for some minutes, the slight excess of bromine was removed by shaking the liquid with a solution of sodium hydrogen sulphite. The nearly colourless liquid, after washing several times with water, was dried with calcium chloride, and the chloroform removed by allowing the liquid to boil under diminished pressure, without the application of external heat. The resulting dibromide was a somewhat dark, heavy oil, the amount obtained being approximately equal to the combined weights of the umbellulone and bromine originally taken for its formation, thus showing that the process is one of addition and not of substitution. A portion was exposed in a vacuum desiccator over paraffin wax, and then analysed:

0.4554 gave 0.528 AgBr.  $Br = 49.3$ .

$C_{10}H_{14}OBr_2$  requires  $Br = 51.6$  per cent.

Umbellulone dibromide is very unstable, readily losing hydrogen bromide even when kept at the ordinary temperature.

##### *Action of Heat on Umbellulone Dibromide. Formation of an Unsaturated Bromoketone, $C_{10}H_{13}OBr$ , and Dibromodihydroumbellulone, $C_{10}H_{14}OBr_2$ .*

A quantity of umbellulone dibromide was slowly heated in a distilling apparatus under 20 mm. pressure. An energetic evolution of hydrogen bromide commenced almost immediately, and a small amount of a colourless liquid passed over into the receiver while the temperature was

below  $100^{\circ}$ . The temperature gradually rose to  $160^{\circ}$ , when the evolution of hydrogen bromide ceased; in the meantime, a large fraction ( $\alpha$ ) had collected in the receiver (pressure = 20 mm.). The residual liquid was then rapidly distilled, and the last distillate, which passed over between  $160^{\circ}$  and  $190^{\circ}/20$  mm., was collected separately from the first fraction, which distilled below  $160^{\circ}$ . A quantity of dark, resinous, undistillable residue remained in the distilling flask. The less volatile fraction, on cooling, became for the most part crystalline, and on diluting with an equal volume of light petroleum, a further amount of the crystalline substance separated. It was collected at the pump and washed with light petroleum. After the removal of the petroleum from the filtrate, the residual oil, together with the more volatile fraction ( $\alpha$ ), when fractionated under diminished pressure yielded a further quantity of the  $\alpha$ -fraction ( $160$ — $190^{\circ}/20$  mm.), which, on treatment with petroleum, afforded more of the crystalline substance, and also two other principal fractions, one of which distilled below  $130^{\circ}/80$  mm., and the other at  $140$ — $145^{\circ}/20$  mm.

*Fraction boiling below  $130^{\circ}/80$  mm.*—This was nearly insoluble in 70 per cent. alcohol, and consisted chiefly of a hydrocarbon; it was distilled repeatedly under the ordinary pressure, and finally twice over sodium, being thus obtained as a colourless, limpid liquid, which boiled at  $175$ — $177^{\circ}$ , had the odour of cymene, and was evidently a hydrocarbon having the formula  $C_{10}H_{14}$ .\*

0.1184 gave 0.3873  $CO_2$  and 0.1125  $H_2O$ .  $C = 89.2$ ;  $H = 10.6$ .  
 $C_{10}H_{14}$  requires  $C = 89.6$ ;  $H = 10.4$  per cent.

*The Unsaturated Bromoketone,  $C_{10}H_{13}OBr$ .*

*Fraction  $140$ — $145^{\circ}/20$  mm.*—This fraction was a heavy, light yellow oil, the vapour of which had a very irritating effect on the eyes. It contained bromine, and was unsaturated, since it instantaneously decolorised a solution of bromine in chloroform.

0.2134 gave 0.4090  $CO_2$  and 0.1168  $H_2O$ .  $C = 52.3$ ;  $H = 6.1$ .  
 0.1593 „ 0.3029  $CO_2$  and 0.0875  $H_2O$ .  $C = 51.9$ ;  $H = 6.1$ .  
 $C_{10}H_{13}OBr$  requires  $C = 52.4$ ;  $H = 5.7$  per cent.

*Action of Zinc Dust and Acetic Acid.*—Fifteen grams of the unsaturated bromoketone were dissolved in 100 c.c. of glacial acetic acid,

\* Sufficient of this hydrocarbon to admit of purification was only obtained by the employment of a large amount of the umbellulone fraction (b. p.  $217$ — $222^{\circ}$ ) (compare this vol., p. 634), afforded by direct fractional distillation of the essential oil of Californian laurel. The formation of a hydrocarbon,  $C_{10}H_{14}$ , would be explained on the assumption that there was associated with the umbellulone a small amount of a substance having the formula  $C_{10}H_{16}O$ .

and 50 grams of zinc dust introduced. A vigorous reduction took place, which was moderated by immersing the flask in cold water. When the reaction had become less energetic, the mixture was heated on the water-bath during 3 hours; the product was then ground up with water and the oil extracted with ether. The ethereal solution was washed successively with water, aqueous sodium carbonate, and water, dried over calcium chloride, and the ether removed. The residual yellow oil was fractionated under the ordinary pressure, when it nearly all passed over between  $212^{\circ}$  and  $218^{\circ}$ , but principally at  $214$ — $217^{\circ}$ , as a nearly colourless liquid, which had an odour closely resembling that of pulegone. A portion of that which distilled at  $214$ — $217^{\circ}$  was analysed:

0.1156 gave 0.3342  $\text{CO}_2$  and 0.1099  $\text{H}_2\text{O}$ .  $\text{C}=78.8$ ;  $\text{H}=10.6$ .

0.1234 „ 0.356  $\text{CO}_2$  „ 0.1174  $\text{H}_2\text{O}$ .  $\text{C}=78.7$ ;  $\text{H}=10.6$ .

$\text{C}_{10}\text{H}_{16}\text{O}$  requires  $\text{C}=79.0$ ;  $\text{H}=10.5$  per cent.

It was thus shown that the action of zinc dust and acetic acid on the unsaturated bromoketone,  $\text{C}_{10}\text{H}_{13}\text{OBr}$ , is to form a ketone having the formula  $\text{C}_{10}\text{H}_{16}\text{O}$ . This new ketone was shown to be saturated, since it did not decolorise a very dilute solution of bromine in chloroform even after some time.

The *semicarbazone*, when prepared in the ordinary way, was first obtained as a viscid oil, which, however, soon became crystalline. It was drained on a porous plate, and then crystallised several times from dilute methyl alcohol, from which it separated in fine, white needles melting at  $171$ — $172^{\circ}$ .

0.051 gave 0.0118  $\text{CO}_2$  and 0.043  $\text{H}_2\text{O}$ .  $\text{C}=63.1$ ;  $\text{H}=9.4$ .

$\text{C}_{10}\text{H}_{19}\text{ON}_3$  requires  $\text{C}=63.1$ ;  $\text{H}=9.1$  per cent.

The semicarbazone is soluble in dilute sulphuric acid (25 per cent.), and on warming the solution it is decomposed, regenerating the pure ketone.

*Dibromodihydroumbellulone*,  $\text{C}_{10}\text{H}_{14}\text{OBr}_2$ .

The crystalline substance which was separated from the less volatile fraction ( $160$ — $190^{\circ}/20$  mm.), obtained as a product of the action of heat on umbellulone dibromide (p. 642), after washing with petroleum, melted at  $118^{\circ}$ ; when recrystallised from warm, light petroleum (b. p.  $40$ — $50^{\circ}$ ), it formed beautiful, white, glistening leaflets melting at  $119$ — $119.5^{\circ}$  without decomposition:

0.123 gave 0.1754  $\text{CO}_2$  and 0.0525  $\text{H}_2\text{O}$ .  $\text{C}=38.9$ ;  $\text{H}=4.7$ .

0.1909 „ 0.2744  $\text{CO}_2$  „ 0.0785  $\text{H}_2\text{O}$ .  $\text{C}=39.2$ ;  $\text{H}=4.6$ .

0.3489 „ 0.4225  $\text{AgBr}$ .  $\text{Br}=51.5$ .

$\text{C}_{10}\text{H}_{14}\text{OBr}_2$  requires  $\text{C}=38.7$ ;  $\text{H}=4.5$ ;  $\text{Br}=51.6$  per cent.

A solution containing 0.5232 gram in 25 c.c. of chloroform gave  $\alpha_D + 0.8'$  in a 1 dm. tube, whence  $[\alpha]_D + 6.4^\circ$ .

Dibromodihydroumbellulone can also be conveniently recrystallised from hot ethyl alcohol; it separates from the solution on cooling in glistening, prismatic needles. It is a saturated substance, since its solution in chloroform containing bromine can be boiled without the colour of the latter becoming discharged. It is also very stable towards boiling nitric acid, for its bromine is not eliminated on boiling with this reagent in the presence of silver nitrate. It does not interact with hydroxylamine even in boiling alcoholic solution.

*Bromodihydroumbellulone*,  $C_{10}H_{15}OBr$ .

Twenty grams of dibromodihydroumbellulone were dissolved in 100 c.c. of glacial acetic acid, and 40 grams of zinc dust added. The mixture was heated on a water-bath during five hours, and then ground up with more glacial acetic acid. The insoluble mixture of zinc salts was then removed by filtration at the pump, and the bromo-derivative precipitated from the filtrate by the addition of water. The crystalline precipitate, when washed, and dried on a porous plate, weighed 13 grams, and then melted at  $58-59^\circ$ . It was recrystallised from dilute methyl alcohol, from which it separated in well-defined, transparent, prismatic needles melting at  $58-59^\circ$ .

0.2042 gave 0.3885  $CO_2$  and 0.1181  $H_2O$ .  $C = 51.9$ ;  $H = 6.4$ .

0.2046 „ 0.3912  $CO_2$  „ 0.1224  $H_2O$ .  $C = 52.1$ ;  $H = 6.6$ .

$C_{10}H_{15}OBr$  requires  $C = 51.9$ ;  $H = 6.5$  per cent.

A solution containing 0.4163 gram in 25 c.c. of chloroform gave  $\alpha_D - 1.10'$  in a 1 dm. tube, whence  $[\alpha]_D - 70.1^\circ$ .

Bromodihydroumbellulone is readily soluble in cold ethyl and methyl alcohols, ethyl acetate, benzene, chloroform, and petroleum. When it is melted and warmed somewhat, its vapour has an odour resembling that of  $\alpha$ -bromocamphor. It is a saturated substance, since its solution in chloroform containing bromine can be boiled without decolorising the latter. Like the dibromo-derivative, bromodihydroumbellulone does not interact with hydroxylamine.

*Tetrahydroumbellulol*,  $C_{10}H_{19}OH$ .

Thirteen grams of bromodihydroumbellulone were dissolved in 150 c.c. of ethyl alcohol, and 10 grams of sodium gradually introduced in small pieces. The solution was not cooled, but was allowed to boil vigorously. When all the sodium had dissolved, the liquid was cooled and diluted with water in order to precipitate the oil, which was then

taken up with ether, the ethereal solution washed with water, dried with calcium chloride, and the ether removed. The residual oil was first distilled under 60 mm. pressure, when it nearly all passed over between  $125^{\circ}$  and  $130^{\circ}$ ; when finally fractionated under the ordinary pressure, the oil passed over for the most part at  $205\text{--}209^{\circ}$ , but boiled most constantly at  $207\text{--}208^{\circ}$  (corr.)/760 mm.; it was thus obtained as a colourless liquid, which had a camphoraceous odour resembling that of borneol.

0.1317 gave 0.3696  $\text{CO}_2$  and 0.1521  $\text{H}_2\text{O}$ .  $\text{C} = 76.5$ ;  $\text{H} = 12.8$ .

0.1305 „ 0.3672  $\text{CO}_2$  „ 0.1512  $\text{H}_2\text{O}$ .  $\text{C} = 76.7$ ;  $\text{H} = 12.9$ .

$\text{C}_{10}\text{H}_{20}\text{O}$  requires  $\text{C} = 76.9$ ;  $\text{H} = 12.8$  per cent.

Sp. gr. = 0.9071 at  $15^{\circ}/15^{\circ}$ .  $[\alpha]_{\text{D}} - 6.6^{\circ}$ .

*Oxidation of Umbellulone with Potassium Permanganate. Formation of a Lactone,  $\text{C}_9\text{H}_{12}\text{O}_2$ .*

Thirty grams of umbellulone were mixed with 500 c.c. of water and the mixture cooled by introducing a few pieces of ice. A 3 per cent. solution of potassium permanganate was then added, with vigorous shaking, so long as the colour of the latter was discharged. It was found that, working in this way, 80 grams of potassium permanganate, which is the equivalent of 4 atomic proportions of oxygen, were required. The liquid, after the removal of the manganese dioxide precipitate, was evaporated to a small volume, acidified with the calculated amount of sulphuric acid, and distilled in steam. The distillate contained a very small amount of an insoluble oil, which had a pleasant, lactonic odour. The cooled acid residue was then saturated with ammonium sulphate, whereupon a quantity of viscid oil separated; this was taken up with ether, the ethereal solution washed once with water, dried with calcium chloride, and the ether removed. The residual viscid oil was then fractionated under 20 mm. pressure. With the exception of a small fraction which passed over below  $170^{\circ}/20\text{ mm.}$ , the whole distilled between  $170^{\circ}$  and  $220^{\circ}$  as a light yellow oil. It was found to be only partly soluble in sodium carbonate solution. Consequently, the whole of the fraction  $170\text{--}220^{\circ}$  was shaken with cold aqueous sodium carbonate and the undissolved portion then taken up with ether. The ethereal solution, after shaking several times with sodium carbonate solution, was washed with water, dried with potassium carbonate, and the ether removed. The residual oil, when fractionally distilled under the ordinary pressure, was ultimately obtained as a nearly colourless liquid boiling at  $217\text{--}221^{\circ}$  and having a pleasant, sweetish, lactonic odour.

0.1269 gave 0.3284  $\text{CO}_2$  and 0.0926  $\text{H}_2\text{O}$ .  $\text{C} = 70.6$ ;  $\text{H} = 8.1$ .

$\text{C}_9\text{H}_{12}\text{O}_2$  requires  $\text{C} = 71.1$ ;  $\text{H} = 7.9$  per cent.

This substance was evidently a lactone, and this conclusion was confirmed by converting it into the barium salt of the corresponding hydroxy-acid. For this purpose, the pure lactone was digested with a concentrated solution of barium hydroxide until all the oil had disappeared. The excess of barium was then removed by means of carbon dioxide. The filtered solution was then evaporated, and finally left in a vacuum desiccator over sulphuric acid. The barium salt was thus obtained as a hard, white cake, which was powdered, dried at  $110^{\circ}$ , and then analysed.

0.2118 gave 0.1033  $\text{BaSO}_4$  instead of 0.1039, which is the calculated amount for  $(\text{C}_9\text{H}_{13}\text{O}_3)_2\text{Ba}$ .

The barium salt is extremely soluble in cold water, and on the addition of silver nitrate to the solution, the silver salt is not precipitated.

The author particularly wishes to reserve the further study of umbellulone and its derivatives.

THE WELLCOME CHEMICAL RESEARCH LABORATORIES,  
LONDON, E.C.

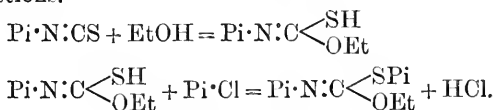
## LXV.—*Picryl Derivatives of Urethanes and Thiourethanes.*

By JAMES CODRINGTON CROCKER, B.A., and FRANK HAROLD LOWE, B.Sc.

In a paper by one of the authors (Trans., 1902, 81, 436), it was shown that picryl chloride reacted readily with ammonium thiocyanate and alcohols, with the production of the alkyl picryl picriminothiocarbonates.

The formation of these compounds was explained by the interaction of an intermediate additive compound of picrylthiocarbimide and picryl chloride with the alcohols. Another explanation of the reaction which, at the time, seemed less probable, when viewed in the light of other researches on the thiocyanates and the work in this paper, seems, however, to be the true one. It was shown by Dixon (Trans., 1899, 75, 375) that the acidic thiocarbimides,  $\text{R}\cdot\text{CO}\cdot\text{N}:\text{C}:\text{S}$ , easily react with the alcohols to form additive compounds, the thiourethanes. When the potassium salts of these substances are treated with alkyl halides, they behave as the tautomeric *pseudothiourethanes*,  $\text{R}\cdot\text{CO}\cdot\text{N}:\text{C}(\text{SH})\cdot\text{OX}$ , and pass into acyl iminothiocarbonic esters,  $\text{R}\cdot\text{CO}\cdot\text{N}:\text{C}(\text{SX}')\cdot\text{OX}$ , the

second alkyl group becoming attached to the sulphur. This explains the formation of the picriminothiocarbonic esters from picryl chloride, thiocyanate, and alcohols. The first formed picrylthiocarbimide unites with the alcohol to form the thiourethane, the tautomeric form of which is again acted on by the picryl chloride, with the production of the picriminothiocarbonate and the liberation of hydrochloric acid—the second molecule of picryl chloride taking the place of the alkyl halide in the foregoing example. According to this explanation, the formation of ethyl picryl picriminothiocarbonate is represented by the following reactions.



The results obtained with *isopropyl*, *tert.*-butyl, and amyl alcohols are described in the present paper.

The reaction with *isopropyl* alcohol is not so complete as in the previous cases. There was a considerable amount of unchanged picryl chloride, and the yield was less than usual. This is probably due to the spatial influence of the two methyl groups in preventing the formation of the thiourethane. With *tert.*-butyl alcohol, this effect is very marked. Even after boiling for an hour under a reflux apparatus, most of the picryl chloride was unchanged, and the sole products isolated were picryl sulphide and picryl thiocyanate, both in rather small quantity. This behaviour of *tert.*-butyl alcohol is very similar to that noticed by Lewis (Proc., 1903, 19, 41) in the case of the reaction between *tert.*-butyl chloride and sodium phenoxide, which gives rise to *tert.*-butylphenol and not the phenyl *tert.*-butyl ether. The amyl compound was obtained by boiling together lead thiocyanate, picryl chloride, benzene, and amyl alcohol. The reaction proceeded normally and gave a moderate yield. Attempts were made to produce the capryl compound, but without result. The bulk of the picryl chloride remained unchanged and very small quantities of picryl thiocyanate and picryl sulphide were isolated.

It seemed of interest to try whether cyanate would react in an analogous manner. The results obtained are quite in accordance with the foregoing explanation of the thiocyanate reaction.

When potassium cyanate is boiled with an alcoholic solution of picryl chloride, two substances are formed.

(1) A substance sparingly soluble in alcohol, having a high melting point, and resembling the picriminothiocarbonates except in colour, which proved to be ethyl picryl picriminocarbonate,  $\text{PiN} : \text{C}(\text{OPi}) \cdot \text{OEt}$ .

(2) A much more fusible substance, moderately easily soluble in alcohol, which was found to be the urethane,  $\text{PiN} : \text{C}(\text{OH}) \cdot \text{OEt}$ .

The ethoxy-group was estimated by Zeisel's method, and the substance was shown to give picramide on hydrolysis. Moreover, it was identical with the compound, melting at 144°, obtained by Romburgh (*Rec. trav. chim.*, 1891, 10, 138) on nitrating phenylurethane. This leaves no doubt as to its constitution.

The formation of these substances is represented by the following equations :  $\text{Pi}\cdot\text{N}:\text{C}:\text{O} + \text{EtOH} = \text{Pi}\cdot\text{N}:\text{C} \begin{smallmatrix} \text{OEt} \\ \text{OH} \end{smallmatrix}$  ;  $\text{Pi}\cdot\text{N}:\text{C} \begin{smallmatrix} \text{OEt} \\ \text{OH} \end{smallmatrix} + \text{Pi}\cdot\text{Cl} = \text{Pi}\cdot\text{N}:\text{C} \begin{smallmatrix} \text{OEt} \\ \text{OPi} \end{smallmatrix} + \text{HCl}$ .

Methyl alcohol under similar conditions also yielded two compounds, the red potassium picrylmethylurethane,  $\text{PiN}:\text{C}(\text{OK})\cdot\text{O}\cdot\text{CH}_3$  (soluble with difficulty in alcohol), and also the free urethane; the former was transformed into the urethane by crystallisation from a mixture of acetic acid and alcohol. This again was identical with Roxburgh's compound melting at 192° (*loc. cit.*).

In addition to these compounds, similar urethanes were prepared from *n*-propyl, *isopropyl*, *isobutyl*, and *amyl* alcohols. *tert*.-Butyl alcohol again behaved abnormally. Picramide was obtained in comparatively large quantities and there was some unchanged picryl chloride, but no urethane was isolated.

The behaviour of these picrylurethanes in solution is rather interesting. The substances themselves and their petroleum, chloroform, and carbon tetrachloride solutions are colourless, but when dissolved in water or alcohol the solutions are intensely yellow. One drop of dilute acid makes the weak solutions colourless, and in the case of water the substance is at once "salted out." When carbon dioxide is passed into a weak alcoholic solution, the colour gradually changes, but is not completely destroyed. On boiling and cooling, the yellow colour again becomes more intense. These marked colour changes, combined with the fact that the substances are excessively weak acids, and therefore not appreciably ionised, seem to indicate that the substances are tautomeric, the solid substances and the petroleum solutions probably containing the urethane proper,  $\text{Pi}\cdot\text{NH}\cdot\text{CO}\cdot\text{OX}$ , whilst other solvents, such as water, alcohol, ether, contain the *pseudourethane*,  $\text{Pi}\cdot\text{N}:\text{C}(\text{OH})\cdot\text{OX}$ .

The production of these urethanes as intermediate compounds between picrylcarbimide and the iminocarbonates confirms the foregoing view with regard to the analogous reaction in the case of thiocyanates.

#### EXPERIMENTAL.

##### *isoPropyl Picryl Picriminothiocarbonate.*

Five grams of picryl chloride and 1.6 grams of ammonium thiocyanate were separately dissolved in the smallest possible amount of

isopropyl alcohol and the hot solutions mixed. Precipitation took place immediately with violent frothing, and an oil which separated became solid on cooling and was collected, washed with water, and then with alcohol; it was then extracted with 20 c.c. of boiling alcohol and the residue crystallised from 40 c.c. of a mixture of alcohol and acetic acids (1:2), filtering from a small quantity of insoluble impurity, the yield of partially purified product being 2.5 grams. After a second crystallisation, it was obtained pure.

0.2299 gave 0.3016  $\text{CO}_2$  and 0.0430  $\text{H}_2\text{O}$ .  $\text{C} = 35.78$ ;  $\text{H} = 2.08$ .

0.2064 „ 31.2 c.c. moist nitrogen at  $16.5^\circ$  and 770 mm.  $\text{N} = 17.83$ .

$\text{C}_{10}\text{H}_{11}\text{O}_{13}\text{N}_7\text{S}$  requires  $\text{C} = 35.49$ ;  $\text{H} = 2.03$ ;  $\text{N} = 18.11$  per cent.

The substance forms light yellow, glistening plates melting at  $147^\circ$ , which are insoluble in water, somewhat sparingly so in alcohol and in ether, and easily dissolve in benzene or glacial acetic acid.

#### *Amyl Picryl Picriminothiocarbonate.*

Ten grams of picryl chloride were mixed with 14 grams of lead thiocyanate and boiled on the water-bath for one hour with a mixture of 80 c.c. of amyl alcohol and 120 c.c. of benzene. The solution was filtered from lead chloride and excess of thiocyanate and the solid residue extracted with benzene, the extracts being mixed with the filtered solution of the product, and the whole liquid then diluted and distilled in steam. The residual solid was washed with alcohol and dried, the yield of the crude product being 9.5 grams. After crystallisation from acetic acid and alcohol (1:1), 6 grams of pure substance were obtained.

0.1795 gave 0.2497  $\text{CO}_2$  and 0.0450  $\text{H}_2\text{O}$ .  $\text{C} = 37.93$ ;  $\text{H} = 2.78$ .

0.1871 „ 27.0 c.c. moist nitrogen at  $17^\circ$  and 772 mm.  $\text{N} = 17.03$ .

$\text{C}_{18}\text{H}_{15}\text{O}_{13}\text{N}_7\text{S}$  requires  $\text{C} = 37.97$ ;  $\text{H} = 2.64$ ;  $\text{N} = 17.23$  per cent.

The compound consists of minute, light yellow, glistening plates melting constantly at  $138.5^\circ$ ; the melting point remaining unchanged after several crystallisations; it is insoluble in water, rather sparingly soluble in alcohol or ether, easily so in acetic acid or benzene.

#### *Picryl Thiocyanate.*

Fifteen grams of picryl chloride and 4.8 grams of ammonium thiocyanate were dissolved separately in the least possible quantity of *tert.*-butyl alcohol and the hot solutions mixed; the precipitate which immediately separates was found to consist, for the most part, of unchanged picryl chloride. It was boiled with water, washed with

alcohol, and then extracted carefully with about 30 c.c. of alcohol and acetic acid (1 : 1). As soon as the melted substance gave place to a light, powdery material, it was filtered off rapidly. The residual crude product, which melted at  $221^{\circ}$ , was a mixture of picryl sulphide and picryl thiocyanate and weighed 3.5 grams. This mixture was now extracted repeatedly with small quantities of alcohol and acetic acid, until the extracts yielded no crystals on cooling. The residue was purified by dissolution in excess of benzyl alcohol and reprecipitation by alcohol. It weighed one gram, and consisted of an almost white powder with a faint yellow tinge, insoluble in water or ether and practically insoluble in acetic acid, benzene, or alcohol. It dissolves readily in acetone or benzyl alcohol, separating from the latter in microscopic, needle-shaped crystals. The substance does not melt, but darkens at about  $285^{\circ}$ .

0.1607 gave 0.1837  $\text{CO}_2$  and 0.0162  $\text{H}_2\text{O}$ .  $\text{C} = 31.18$ ;  $\text{H} = 1.12$ .

0.1741 „ 31.0 c.c. moist nitrogen at  $20^{\circ}$  and 760 mm.  $\text{N} = 20.61$ .

0.2145 „ 0.1992  $\text{BaSO}_4$ .  $\text{S} = 12.18$ .

$\text{C}_7\text{H}_2\text{O}_6\text{N}_4\text{S}$  requires  $\text{C} = 31.11$ ;  $\text{H} = 0.74$ ;  $\text{N} = 20.74$ ;  $\text{S} = 11.85$  per cent.

The crystals obtained by extracting the crude product were found to be picryl sulphide; when recrystallised, they melted at  $226^{\circ}$ , and did not depress the melting point of the substance prepared according to Willgerodt's method. It was rather remarkable that, when boiled with caustic potash, picryl sulphide yielded ammonia and also alkali nitrite. The production of ammonia was found to be due to the interaction of nitrite and potassium picrate formed in the reaction, as these substances, when boiled with potash, were found to yield ammonia.

### *Picrylmethylurethane.*

Nine grams of picryl chloride and 3 grams of potassium cyanate were mixed with 90 c.c. of methyl alcohol, heated on the water-bath for 3 hours in a reflux apparatus, and filtered hot; the filtrate, on cooling, deposited yellow crystals, which were washed with water and recrystallised from ethyl alcohol and acetic acid (2 : 1). The long needles obtained, which were almost colourless, melted at  $192^{\circ}$  and seemed to be identical with Romburgh's compound (*loc. cit.*).

The red residue was insoluble in alcohol, but dissolved easily in glacial acetic acid, changing colour, and depositing the same colourless crystals, the yield being 7 grams. As it was important to demonstrate that this really was the picrylurethane, it was analysed and the methoxy-group determined by Hewitt's modification of Zeisel's method (*Trans.*, 1902, 81, 319).

- 0.2004 gave 0.2476  $\text{CO}_2$  and 0.0400  $\text{H}_2\text{O}$ .  $\text{C} = 33.71$ ;  $\text{H} = 2.18$ .  
 0.1909 „ 33.8 c.c. moist nitrogen at  $25^\circ$  and 750 mm.  $\text{N} = 19.75$ .  
 $\text{C}_8\text{H}_6\text{O}_8\text{N}_4$  requires  $\text{C} = 33.57$ ;  $\text{H} = 2.09$ ;  $\text{N} = 19.58$  per cent.  
 0.2236 gave 0.1671 AgI.  $\text{OMe} = 9.86$ .  
 $\text{C}_8\text{H}_6\text{O}_8\text{N}_4$  requires  $\text{OMe} = 10.08$  per cent.

Hydrolysis of the substance by hydrochloric or acetic acid yielded picramide melting at  $188^\circ$ .

The red residue, which was insoluble in alcohol, was recrystallised from water; it was found to contain potassium, the analysis corresponding with the mono-potassium salt described by Romburgh (*loc. cit.*).

- 0.3595 gave 0.0975  $\text{K}_2\text{SO}_4$ .  $\text{K} = 12.16$ .  
 $\text{C}_8\text{H}_5\text{O}_8\text{N}_4\text{K}$  requires  $\text{K} = 12.04$  per cent.

This salt was partially hydrolysed by water, and was distinctly alkaline to litmus.

The conductivity of the methylurethane was determined. Owing to the small solubility at the ordinary temperature, the indications were too small to be of value. It was therefore taken in saturated solution at  $75.6^\circ$ . This gave  $\mu_{580} = 4.33$ , whilst a solution of the potassium salt in a saturated solution of the methyl compound under the same conditions gave  $\mu_{110} = 207.2$ . This indicates that the acid is weaker than carbonic acid, giving  $\mu_\infty = 590$ , and  $\text{K} = 0.0793$ .

*Ethyl Picryl Picriminocarbonate and Picrylethylurethane.*

Nine grams of picryl chloride were mixed with 3 grams of potassium cyanate and 70 c.c. of absolute alcohol, the whole being boiled in a reflux apparatus for 3 hours and then filtered while hot. The residue, which amounted to 0.6 gram, was washed with alcohol and water in order to remove potassium cyanate; it was practically insoluble in alcohol, ether, or water; easily soluble in benzene, and also in glacial acetic acid, from which it crystallised in minute, heavy, almost colourless crystals melting at  $222^\circ$ .

- 0.1972 gave 0.2560  $\text{CO}_2$  and 0.0342  $\text{H}_2\text{O}$ .  $\text{C} = 35.40$ ;  $\text{H} = 1.93$ .  
 $\text{C}_{15}\text{H}_9\text{O}_{14}\text{N}_7$  requires  $\text{C} = 35.23$ ;  $\text{H} = 1.76$  per cent.

The hot filtrate deposited the picrylethylurethane (*loc. cit.*) either in plates or needles, which were shown to be dimorphous, both forms of crystals melting at  $147^\circ$ ; the yield was 6 grams. The needles separate from dilute alcoholic solution, and the plates from concentrated solutions. As with the other urethanes, the aqueous and alcoholic solutions are intensely coloured, but are decolorised by the addition of one drop of dilute acid.

0.2076 gave 0.2764  $\text{CO}_2$  and 0.0521  $\text{H}_2\text{O}$ .  $\text{C} = 36.30$ ;  $\text{H} = 2.79$ .

0.1694 ,, 26.8 c.c. moist nitrogen at  $14^\circ$  and 770 mm.  $\text{N} = 18.46$ .

$\text{C}_9\text{H}_8\text{O}_8\text{N}_4$  requires  $\text{C} = 36.00$ ;  $\text{H} = 2.66$ ;  $\text{N} = 18.66$  per cent.

0.1399 gave 0.1101  $\text{AgI}$ .  $\text{OEt} = 15.19$ .

$\text{C}_9\text{H}_8\text{O}_8\text{N}_4$  requires  $\text{OEt} = 15.00$  per cent.

### *Picryl-n-propylurethane.*

Five grams of picryl chloride, 1.6 grams of potassium cyanate, and 17 c.c. of *n*-propyl alcohol with 20 c.c. of benzene were boiled together for 3 hours. The benzene and *n*-propyl alcohol were distilled off in steam, and the solid residue recrystallised from a mixture of ethyl alcohol and glacial acetic acid (3:1). Well-defined, almost colourless needles melting at  $139^\circ$  were obtained, the yield being 3 grams. The substance is slightly soluble in water or light petroleum, moderately so in alcohol or ether, easily so in benzene, glacial acetic acid, or alcohol.

0.3356 gave 0.4682  $\text{CO}_2$  and 0.0979  $\text{H}_2\text{O}$ .  $\text{C} = 38.06$ ;  $\text{H} = 3.24$ .

0.2245 ,, 33.8 c.c. moist nitrogen at  $15^\circ$  and 760.5 mm.  $\text{N} = 17.63$ .

$\text{C}_{10}\text{H}_{10}\text{O}_8\text{N}_4$  requires  $\text{C} = 38.23$ ;  $\text{H} = 3.19$ ;  $\text{N} = 17.83$  per cent.

### *Picrylisopropylurethane.*

A mixture of 2.5 grams of picryl chloride, 0.8 gram of potassium cyanate, and 20 c.c. of *isopropyl* alcohol was boiled for two hours in a reflux apparatus and then cooled; the crystalline product, which was collected, washed with hot water and alcohol, weighed 2.2 grams. When crystallised from a mixture of acetic acid and alcohol (1:1) and then from dilute acetic acid, it forms long, white, lustrous needles melting at  $177.5^\circ$ , which are slightly soluble in hot water, forming a yellow solution. The substance is easily soluble in acetic acid and in benzene, moderately so in alcohol or ether, somewhat sparingly so in light petroleum. When boiled with caustic potash, ammonia is evolved. If to the yellow aqueous solution a drop of dilute acid is added, it is immediately decolorised and the substance is salted out.

0.1907 gave 0.2673  $\text{CO}_2$  and 0.0574  $\text{H}_2\text{O}$ .  $\text{C} = 38.22$ ;  $\text{H} = 3.34$ .

0.2070 ,, 31.6 c.c. moist nitrogen at  $16.5^\circ$  and 754 mm.  $\text{N} = 17.62$ .

$\text{C}_{10}\text{H}_{10}\text{O}_8\text{N}_4$  requires  $\text{C} = 38.22$ ;  $\text{H} = 3.19$ ;  $\text{N} = 17.84$  per cent.

### *Picrylisobutylurethane.*

Five grams of picryl chloride and 1.6 grams of potassium cyanate were boiled on the water-bath for two hours with a mixture of 20

c.c. of *isobutyl* alcohol and 20 c.c. of benzene. The mixture was then distilled in steam and the residue crystallised from a mixture of alcohol and acetic acid. On cooling, the solution became nearly solid. The product when collected and washed with alcohol, weighed 2·3 grams; it was crystallised from dilute acetic acid, and separated in nearly colourless, lustrous needles with a faint yellow tinge (m. p.  $134^{\circ}$ ). It is moderately soluble in hot water, giving a yellow solution, and dissolves easily in acetic acid, alcohol, or benzene. It is moderately soluble in light petroleum or ether. When boiled with caustic potash solution, ammonia and *isobutyl* alcohol are evolved, but the substance may be crystallised practically unchanged from sodium carbonate solution. The solutions in water, alcohol, ether, acetic acid, and benzene are all somewhat yellow, particularly the aqueous and alcoholic solutions. The solution in light petroleum, however, is quite colourless. On the other hand, the addition of one drop of hydrochloric or acetic acid to the alcoholic or aqueous solution removes the colour. Carbon dioxide also produces this effect, but the colour returns on expelling the gas.

0·2396 gave 0·3530  $\text{CO}_2$  and 0·0842  $\text{H}_2\text{O}$ .  $\text{C} = 40\cdot18$ ;  $\text{H} = 3\cdot90$ .

0·1955 „ 29·0 c.c. moist nitrogen at  $15^{\circ}$  and 752 mm.  $\text{N} = 17\cdot20$ .

$\text{C}_{11}\text{H}_{12}\text{O}_8\text{N}_4$  requires  $\text{C} = 40\cdot25$ ;  $\text{H} = 3\cdot66$ ;  $\text{N} = 17\cdot08$  per cent.

#### *Picrylamylurethane.*

Five grams of picryl chloride and 1·6 grams of potassium cyanate were mixed with 40 c.c. of amyl alcohol and heated on the water-bath for 12 hours; on cooling, the whole mass solidified. The excess of amyl alcohol was removed by distillation in steam and the residue crystallised several times from a mixture of ethyl alcohol and glacial acetic acid (1 : 1) and finally from ethyl alcohol alone; the yield was 2·5 grams. The needle-shaped, somewhat yellow crystals, which melted at  $131^{\circ}$ , were moderately soluble in hot water or light petroleum and easily so in alcohol, benzene, ether, or acetic acid. As in the case of the other urethanes, the solution in light petroleum is colourless, whilst the other solutions are more or less yellow, particularly the aqueous and alcoholic solutions.

0·2689 gave 0·4139  $\text{CO}_2$  and 0·1088  $\text{H}_2\text{O}$ .  $\text{C} = 42\cdot11$ ;  $\text{H} = 4\cdot49$ .

0·1964 „ 28·4 c.c. moist nitrogen at  $22^{\circ}$  and 754·3 mm.  $\text{N} = 16\cdot25$ .

$\text{C}_{12}\text{H}_{14}\text{O}_8\text{N}_4$  requires  $\text{C} = 42\cdot11$ ;  $\text{H} = 4\cdot09$ ;  $\text{N} = 16\cdot38$  per cent.

*tert.*-Butyl alcohol behaved abnormally, as before; when treated in the usual way, picramide alone was obtained in somewhat large quantity.

The authors wish to take this opportunity of thanking Professor J. B. Coleman for his kindness in placing the resources of the laboratory at their disposal.

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LXVI.—*Experiments on the Synthesis of the Terpenes.*  
*Part I. Synthesis of Terpin, Inactive Terpeneol,*  
*and Dipentene.*

By WILLIAM HENRY PERKIN, jun.

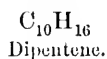
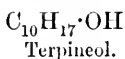
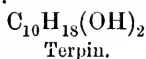
IN that remarkable section of chemistry which deals with the terpenes and their derivatives, there are probably few substances of greater importance than the closely related group, terpin, terpeneol, and dipentene, and this is due, not only to the great interest attached to the substances themselves, but also to their intimate connection with pinene and many other members of the same section. Terpin, as is well known, combines very readily with water to form the highly characteristic compound, terpin hydrate,  $C_{10}H_{18}(OH)_2 \cdot H_2O$ , and from the first this hydrate has been specially selected by chemists for investigation, partly because of its extraordinary facility for crystallising and the consequent ease with which it is obtained pure from oil of turpentine, and partly because there was reason to suppose that the determination of its constitution would afford a valuable clue to the nature of the terpene group as a whole. The fact that the constitution of terpin and its derivatives is now fairly well understood is due principally to the laborious researches of Baeyer, Tilden, Tiemann and Schmidt, and Wallach, and to the brilliant theoretical deductions of Wagner, and to such of this work as has a direct bearing on the present investigation some mention is made below.

It must, however, be remembered that it is impossible, within the limits of a paper of this kind, to enter into anything like a complete historical discussion of the gradual progress of the development of the formulæ of terpin, terpeneol, and dipentene, and for this reason many valuable contributions to our knowledge of the subject must unavoidably remain unnoticed.

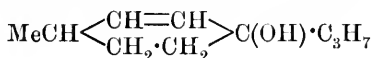
The difficulties which early investigators of terpin and its derivatives had to encounter were of a quite unusual kind, not only owing to the fact

that the chemical behaviour of the many partially unsaturated closed chain compounds belonging to this class was, at that time, not at all understood, but also because of the unexpected fundamental intra-molecular changes which were frequently met with, and which gave rise to false deductions and the suggestion of many formulæ now known to be incorrect.

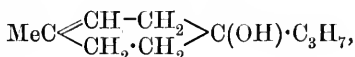
That a close relationship exists between terpin, terpineol, and dipentene was long ago evident from the work of Tilden (*Ber.*, 1879, 12, 848) and of Wallach (*Annalen*, 1885, 230, 258), who showed that when terpin is digested with dilute acids, it yields terpineol, and that the latter is converted by potassium hydrogen sulphate at 200° into dipentene, these changes being simply due to the successive elimination of water :



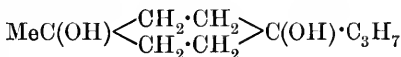
The first to represent terpineol as a derivative of cymene appears to have been Kanonnikoff (*J. Russ. Phys. Chem. Soc.*, 1883, 15, 472), who, mainly from physical considerations, proposed the formula



for this substance. In a remarkable paper (*Annalen*, 1893, 277, 105), which contains a careful investigation of terpineol, Wallach suggested the following modification of this formula,



and, shortly afterwards, Baeyer (*Ber.*, 1893, 26, 2558) published a research on the same subject, in which he expresses his agreement with Wallach's view of the constitution of terpineol, and at the same time suggests the formula

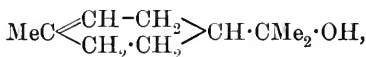


for terpin.

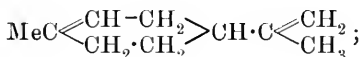
The strongest argument against the acceptance of these views was the fact that, in whichever way water is eliminated from Wallach's terpineol formula, a constitution for dipentene is arrived at which does not contain an asymmetric carbon atom, whereas it is well known that dipentene is an externally compensated mixture of the two active *d*- and *l*-limonenes. In order to get over this difficulty, Baeyer (*Ber.*, 1894, 27, 454) suggested the possibility that the activity of the limonenes was due to the asymmetry of the whole molecule, and not to the presence of an asymmetric carbon atom.

In 1894, Wagner published his classical paper "On the oxidation of

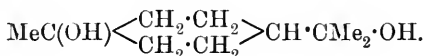
cyclic compounds" (*Ber.*, 27, 1636), in which he discusses the constitutions of some of the more important members of the terpene group. From a careful consideration of the relationship of terpineol to pinene, pinol, and sobrerol, he deduces the expression,



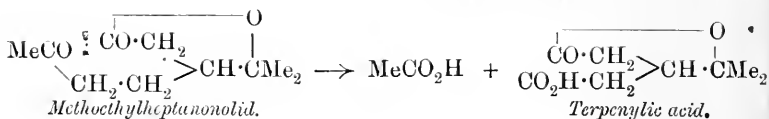
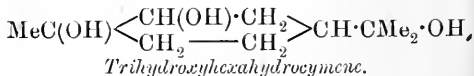
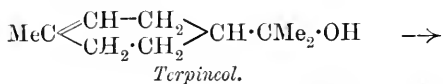
as best representing terpineol, and points out that, if this formula is adopted, the difficulty with regard to the activity of the limonenes disappears, since the constitution of limonene (dipentene) would then be represented thus :



that is to say, by a formula which contains an asymmetric carbon atom. The constitution of terpin itself, deduced from the above formula for terpineol, would then be



That the formula suggested by Wagner for terpineol is correct was rendered probable by the subsequent work of Wallach (*Ber.*, 1895, 28, 1776), who showed that this substance, on oxidation, is converted first into trihydroxyhexahydrocymene, which then breaks up further into a ketolactone, called methoethylheptanonolid, and then into acetic and terpenylic acids. With the aid of Wagner's formula, these changes may be expressed in the following simple manner :

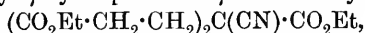


but Wallach is careful to remark that the formation of these oxidation products cannot be accepted as a definite proof that the constitution of terpineol is that suggested by Wagner.

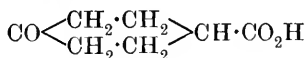
The present investigation was undertaken with the object of synthesising terpin, terpineol, and dipentene, not only on account of the interest which always attaches to syntheses of this kind, but also in the hope that a method of synthesis might be devised of such a

simple kind that there would no longer be room for doubt as to the constitution of these important substances.

In the synthesis described in this paper, the first step was the preparation of ethyl  $\gamma$ -cyanopentane- $\alpha\gamma\epsilon$ -tricarboxylate,

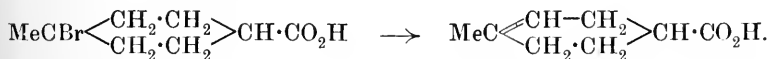


by the interaction of ethyl  $\beta$ -iodopropionate and ethyl sodiocyanoacetate. On hydrolysis with hydrochloric acid, this ester yields pentane- $\alpha\gamma\epsilon$ -tricarboxylic acid, and on digesting with acetic anhydride and distilling, this acid is decomposed, with elimination of water and carbon dioxide and formation of  $\delta$ -ketohexahydrobenzoic acid,

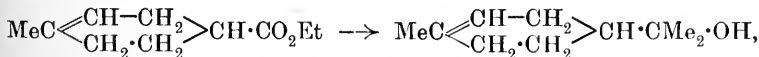


(compare *Trans.*, 1904, 85, 418).

The ester of this acid reacts readily with magnesium methyl iodide in ethereal solution, and the product, on hydrolysis, yields  $\delta$ -hydroxyhexahydro-*p*-toluic acid,  $\text{MeC}(\text{OH}) \begin{array}{c} \text{CH}_2\cdot\text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2\cdot\text{CH}_2 \end{array} \text{CH}\cdot\text{CO}_2\text{H}$ , which melts at  $153^\circ$  and has already been prepared by Stephan and Helle (*Ber.*, 1902, 35, 2156) by the oxidation of  $\Delta^{(9)}$ -menthenol (I) (see p. 659). This hydroxy-acid dissolves readily in fuming hydrobromic acid, and the solution soon deposits crystals of  $\delta$ -bromohexahydro-*p*-toluic acid (m. p.  $126^\circ$ ), from which, by treatment with weak alkalis or pyridine,  $\Delta^3$ -tetrahydro-*p*-toluic acid (m. p.  $99^\circ$ ) is obtained,



The last step was to convert the unsaturated acid into its ester and to act on this with an ethereal solution of magnesium methyl iodide, when an almost quantitative yield of an oil was obtained which, on examination, proved to be *terpineol*. This synthesis is readily understood with the aid of the formulæ,



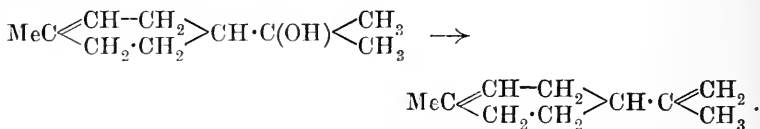
the change being simply the conversion of the  $-\text{CO}_2\text{Et}$  group into the group  $-\text{CMe}_2\cdot\text{OH}$ .

The *terpineol* thus synthesised had the pronounced odour of lilac which is so characteristic of this substance, and distilled constantly at  $135^\circ$  under 60 mm. pressure, and this was found to be exactly the temperature at which a sample of pure *terpineol*, from Schimmel & Co., distilled in the same apparatus and under the same conditions.

In order that there might be no room for doubt as to the identity of the synthetical product, it was converted into the *nitrosochloride*,

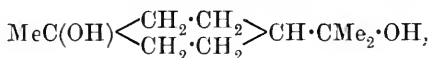
$C_{10}H_{15}O, NOCl$  (m. p.  $122^\circ$ ), and *phenylurethane*,  $C_{10}H_{17}O \cdot CO \cdot NH \cdot C_6H_5$  (m. p.  $113^\circ$ ), and these were compared with specimens prepared from ordinary terpineol, with the result that the preparations obtained from both sources were found to be absolutely identical.

The next step was to convert the synthetical terpineol into dipentene, which was readily accomplished by heating with potassium hydrogen sulphate, when water was eliminated according to the scheme,



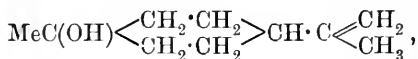
The *dipentene* produced in this way was converted into the *tetra-bromide*,  $C_{10}H_{16}Br_4$  (m. p.  $125^\circ$ ), the *dihydrochloride*,  $C_{10}H_{16}, 2HCl$  (m. p.  $48-50^\circ$ ), and the *nitrosochloride*,  $C_{10}H_{16}, NOCl$  (m. p.  $106^\circ$ ), and these derivatives were compared with the corresponding specimens obtained from ordinary dipentene, with which they were found to be identical in all respects.

Lastly, the synthetical terpineol was agitated with dilute sulphuric acid until the oil had become converted into a mass of crystals; these, on examination, were found to consist of pure terpin hydrate,

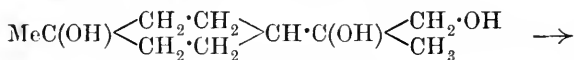


and thus the synthesis of the three substances, terpin, terpineol, and dipentene, which have played so prominent a part in the history of the terpene group, was accomplished, and in a way which can leave no further doubt as to their constitutions.

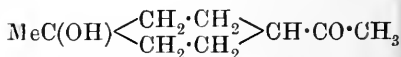
Recently, Stephan and Helle (*Ber.*, 1902, 35, 2147) have shown that one of the products of the dehydration of terpin is that isomeric modification of terpineol,



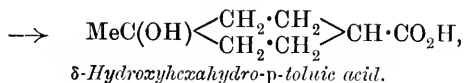
for which the name  $\Delta^{(9)}$ -menthenol (1) has been suggested (Meyer and Jacobson, *Lehrbuch*, II, 933). When this interesting substance is oxidised, it yields the following products



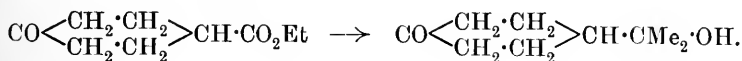
*Trihydroxyhexahydrocymene.*



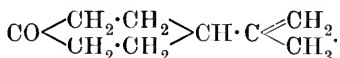
*p-Hydroxy-p-methylhexahydroacetophenone.*



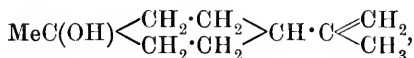
and the last of these is identical with the acid which is one of the steps in the foregoing synthesis of terpineol. For the purpose of this synthesis, this acid was prepared from ethyl  $\delta$ -keto-hexahydrobenzoate by the action of magnesium methyl iodide, the change being simply due to the conversion of the ketonic group into the group  $\text{MeC(OH)}\langle$ . The reaction does not, however, proceed entirely in this direction, for there is always produced, although in very small quantity, a neutral oil, the formation of which is due to the conversion of the  $-\text{CO}_2\text{Et}$  group into the group  $-\text{CMe}_2 \cdot \text{OH}$  :\*



The hydroxyisopropyl-*p*-keto-hexamethylene obtained in this way could only be somewhat imperfectly investigated, owing to the small amount of available material. It distils at  $177-180^\circ$  under 100 mm. pressure, and when treated with hydrobromic acid and then with alcoholic potash, is converted into isopropenyl-*p*-keto-hexamethylene (b. p.  $186^\circ$ ) :



When this ketone is left in contact with magnesium methyl iodide, a substance,  $\text{C}_{10}\text{H}_{18}\text{O}$ , is produced, which distils at  $127^\circ$  (60 mm.) and crystallises on cooling. Assuming that, during this process, the ketonic group is converted in the usual way into the group  $\text{MeC(OH)}\langle$ , the substance,  $\text{C}_{10}\text{H}_{18}\text{O}$ , should be identical with the menthenol,

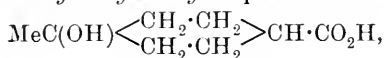


of Stephan and Helle. The most characteristic derivative of this menthenol appears to be the phenylurethane which melts at  $85^\circ$ , and, on preparing this derivative from the above synthetical substance, crystals were obtained which melted at  $83-85^\circ$ , so that there is little room for doubt that the synthetical substance is identical with the above  $\Delta^{8(9)}$ -menthenol (1).

It is hoped that further experiments, which are in progress, will result in the synthesis of other important members of the terpene series.

\* This behaviour has been also observed in the case of other keto-esters, and a description of the interesting substances obtained in this way is reserved for a future communication.

*cis*- $\delta$ -Hydroxyhexahydro-*p*-toluic Acid,



and its Lactone.

The preparation of these substances may be conveniently carried out in the following way.

In a large flask, connected with a reflux condenser, magnesium (12 grams) is covered with anhydrous ether \* (300 c.c.), and then methyl iodide (100 grams) added in four portions, the vigorous reaction being kept under control by means of running water. As soon as all the magnesium has dissolved, the flask is well cooled, and ethyl  $\delta$ -keto-hexahydrobenzoate † (50 grams) is then gradually run in. The decomposition is not energetic, the rise of temperature being comparatively small, and as this seemed to point to the reaction being a gradual one, the whole was always left for 24 hours.

Excess of dilute hydrochloric acid is then cautiously added in small quantities at a time, the flask being carefully cooled after each addition, the ethereal solution is separated, washed with a little water and evaporated, and the residual yellow oil mixed with a solution of caustic potash (50 grams) in methyl alcohol. After heating for a few minutes on the water-bath, water is added, and the small quantity of neutral oil (the examination of which is described on p. 670) extracted with ether.

The aqueous liquor is then evaporated until free from methyl alcohol, transferred to a flask, acidified with hydrochloric acid, and heated for half an hour on the water-bath, when the crude lactone of  $\delta$ -hydroxyhexahydro-*p*-toluic acid separates as a brown oil which has a powerful odour of peppermint. In order to extract completely the whole of the products of the reaction, the aqueous liquors must be treated at least 20 times with ether in the ordinary way or 10 times on the shaking machine: the ethereal solution is then repeatedly extracted with sodium carbonate (A, see p. 661), dried over calcium chloride, and evaporated. The residual crude lactone distils for the most part at 140—150° under 45 mm. pressure and the distillate gradually becomes semi-solid. After cooling in ice and salt, the crystals are rapidly collected at the pump, ‡ drained on porous porcelain, and purified by recrystallisation

\* The ether used in these experiments was first dehydrated over sodium and then distilled over phosphoric oxide; the methyl iodide was also distilled over phosphoric oxide.

† For the preparation of this ester, see Trans., 1904, 85, 427.

‡ The oily filtrate from these crystals may be used, without further purification, in the preparation of  $\delta$ -bromohexahydro-*p*-toluic acid (p. 663).

from light petroleum (b. p. 60—70°), from which the lactone separates in glistening leaflets.

0.1240 gave 0.3098 CO<sub>2</sub> and 0.0962 H<sub>2</sub>O. C=68.2; H=8.6.

0.1363 „ 0.3421 CO<sub>2</sub> „ 0.1061 H<sub>2</sub>O. C=68.4; H=8.7.

C<sub>8</sub>H<sub>12</sub>O<sub>2</sub> requires C=68.6; H=8.6 per cent.

The lactone of *cis*- $\delta$ -hydroxyhexahydro-*p*-toluic acid has already been described by Stephan and Helle (*Ber.*, 1902, 35, 2154); it melts at 69—70°, and possesses a penetrating odour closely resembling that of thymol. When the lactone is warmed with barium hydroxide, it readily dissolves, and the solution, after acidifying, remains clear, but if boiled with excess of hydrochloric acid, oily drops of the lactone soon separate. In order to isolate the corresponding hydroxy-acid, a considerable quantity of the lactone was hydrolysed by boiling with excess of barium hydroxide, the acidified solution being then extracted 10 times with ether. After drying over calcium chloride and evaporating to a small bulk, the ethereal solution gradually deposited a crystalline crust, which was collected, washed with a little ether, and re-crystallised from the same solvent.

0.1395 gave 0.3099 CO<sub>2</sub> and 0.1143 H<sub>2</sub>O. C=60.5; H=9.1.

C<sub>8</sub>H<sub>14</sub>O<sub>3</sub> requires C=60.8; H=8.8 per cent.

*cis*- $\delta$ -Hydroxyhexahydro-*p*-toluic acid melts at about 153°, and is readily soluble in hot water, from which it crystallises, on cooling, in colourless, glistening leaflets.

#### *Examination of the Sodium Carbonate Extract A* (see p. 660).

After the lactone of  $\delta$ -hydroxyhexahydro-*p*-toluic acid had been separated as described above, the extract (A) was acidified, saturated with ammonium sulphate, and extracted 10 times with ether; the ethereal solution was dried over calcium chloride and evaporated, when a brown syrup was obtained, which, when left over sulphuric acid in a vacuum desiccator, became semi-solid. In contact with porous porcelain, the dark, oily impurity was soon absorbed, and the residual yellow, crystalline mass was readily purified by crystallisation from water with the aid of animal charcoal. The colourless, glistening crystals thus obtained melted at 153°, and consisted of pure  $\delta$ -hydroxyhexahydro-*p*-toluic acid.

0.1401 gave 0.3112 CO<sub>2</sub> and 0.1140 H<sub>2</sub>O. C=60.6; H=9.0.

C<sub>8</sub>H<sub>14</sub>O<sub>3</sub> requires C=60.8; H=8.8 per cent.

The amount of hydroxy-acid obtained in this way was considerable (p. 662), and it is therefore evident that only a portion of this acid is

converted into its lactone when it is digested with dilute hydrochloric acid under the conditions described on p. 660.

The porous porcelain, which had been used to absorb the dark, oily mother liquors of the hydroxy-acid (see above), was broken up and extracted with ether in a Soxhlet apparatus, and the extract dried over calcium chloride and evaporated. On distilling the residue under 15 mm. pressure, water was eliminated, and, with the exception of a small quantity of a dark brown, resinous substance, the whole passed over below  $210^{\circ}$ , and most of it distilled at  $140-150^{\circ}$ . The distillate was dissolved in ether, the ethereal solution extracted with sodium carbonate, dried over calcium chloride, and evaporated, and the residue fractionated under 100 mm. pressure, when the whole passed over at  $175-185^{\circ}$  as a colourless oil, which gradually became semi-solid, and on examination was found to consist of the lactone of  $\delta$ -hydroxyhexahydro-*p*-toluic acid.\*

The sodium carbonate extract was acidified and extracted, when, after drying and evaporating to a small bulk, small hexagonal plates were deposited which melted at  $65-67^{\circ}$ , and consisted of  $\delta$ -keto-hexahydrobenzoic acid, which had escaped the action of the magnesium methyl iodide, and in some experiments a good deal of this valuable acid was recovered in this way. In order to obtain an approximate estimate of the yields obtained in the above preparation of  $\delta$ -hydroxyhexahydro-*p*-toluic acid and its lactone, two special experiments were made, and the average of these gave the following results. After treatment with magnesium methyl iodide, 100 grams of ethyl keto-hexahydrobenzoate were found to yield 21 grams of lactone (obtained direct), and, from the sodium carbonate extract (A), 12 grams of the same lactone, 10 grams of the hydroxy-acid, and 8 grams of unchanged keto-hexahydrobenzoic acid. No doubt the considerable loss shown by these numbers is partly accounted for by the formation of resinous substances which remain in the distilling flasks, but it is also due largely to the great difficulty experienced throughout this research in extracting completely the products of the reactions, even when the solutions were treated on the shaking machine with large quantities of ether.

The  $\delta$ -hydroxyhexahydro-*p*-toluic acid described in this section is evidently the *cis*-modification, since it readily yields a lactone, and, in spite of very careful search, no trace of the corresponding *trans*-acid, which it was thought should also have been present, could be detected.

\* Stephan and Helle (*loc. cit.*, p. 2153) state that pure  $\delta$ -hydroxyhexahydro-*p*-toluic acid distils unchanged under 10-15 mm. pressure, but yields the lactone when distilled under the ordinary pressure.

The above experiment shows that the crude acid is completely converted into its lactone on distillation under 15 mm. pressure.

Attention has already been directed (Trans., 1904, 85, 421) to the fact that in many cases where stereoisomeric modifications should be capable of existence it sometimes happens either that, as in the above case, only one of the modifications is actually obtained, or more frequently that the one is found to be present in very much larger quantities than the other.

*δ-Bromohexahydro-p-toluic Acid*,  $\text{MeCBr} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{CH} \cdot \text{CO}_2\text{H}$ , and

*Δ<sup>3</sup>-Tetrahydro-p-toluic Acid*,  $\text{MeC} \begin{smallmatrix} \text{CH} - \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{CH} \cdot \text{CO}_2\text{H}$ , and its

*Derivatives.*

When the finely powdered lactone of *δ*-hydroxyhexahydro-*p*-toluic acid (p. 661) was mixed with aqueous hydrobromic acid (saturated at 0°) it dissolved, and almost immediately the liquid became clouded and an oil separated which rapidly solidified. After two hours, water was added, the crystalline precipitate of the bromo-acid collected, and left in contact with porous porcelain until quite dry; it was then dissolved in boiling light petroleum (b. p. 70–80°), from which it separated in groups of glistening needles. The dry substance has a satiny lustre, and closely resembles benzoic acid in appearance.

0.1368 gave 0.1156 AgBr. Br = 36.0.

$\text{C}_8\text{H}_{13}\text{O}_2\text{Br}$  requires Br = 36.2 per cent.

*δ-Bromohexahydro-p-toluic acid* softens at 122° and melts at about 126°; it is readily soluble in alcohol, but almost insoluble in water; it dissolves readily in boiling light petroleum, but sparingly in the cold. Much of the bromo-acid which was required for this research was prepared direct from *δ*-hydroxyhexahydro-*p*-toluic acid itself. This acid dissolves in concentrated hydrobromic acid, but the solution soon begins to deposit crystals, and, after two hours, water is added and the bromo-acid purified as described above. Again, in preparing the bromo-acid from the lactone, it should be mentioned that it is not at all necessary to use the recrystallised lactone; the semi-solid fraction boiling at 140–150° (45 mm.) was always employed with excellent results (compare p. 660 and footnote).

*Action of Sodium Carbonate on δ-Bromohexahydro-p-toluic Acid.*—In studying this decomposition, the pure bromo-acid was ground with water to a fine paste, excess of a warm saturated solution of sodium carbonate was then added, and, after the acid had dissolved, the whole was heated to boiling for a few minutes. On acidifying the cold liquid, a crystalline precipitate separated at once and was collected, washed well, and purified by recrystallisation from much water, from which the substance separated in needles resembling benzoic acid.

0.1258 gave 0.3162  $\text{CO}_2$  and 0.0980  $\text{H}_2\text{O}$ .  $\text{C} = 68.5$ ;  $\text{H} = 8.6$ .

0.1513 „ 0.3795  $\text{CO}_2$  „ 0.1179  $\text{H}_2\text{O}$ .  $\text{C} = 68.4$ ;  $\text{H} = 8.7$ .

$\text{C}_8\text{H}_{12}\text{O}_2$  requires  $\text{C} = 68.6$ ;  $\text{H} = 8.6$  per cent.

This  $\Delta^3$ -tetrahydro-*p*-toluic acid has already been obtained by Stephan and Helle (*Ber.*, 1902, 35, 2154) from  $\Delta^{8(9)}$ -menthenol (1) by the action of oxidising agents. It softens at  $95^\circ$  and melts at  $99$ – $100^\circ$ ; it is almost insoluble in cold water, and very sparingly so even on boiling; it dissolves readily in acetic acid, and dilute acetic acid appears to be the most convenient solvent from which to crystallise it.

The aqueous mother liquors from which this acid had separated on acidifying were extracted repeatedly with ether, the ethereal solution dried over calcium chloride and evaporated, when a considerable quantity of a solid acid was obtained which crystallised from water in glistening needles and melted at  $153^\circ$ . This substance on analysis proved to be  $\delta$ -hydroxyhexahydro-*p*-toluic acid, which had evidently been produced from the bromo-acid by simple hydrolysis.

*Action of Pyridine on  $\delta$ -Bromohexahydro-*p*-toluic Acid.*—As the yield of the tetrahydro-acid produced in the above experiment was only about 60 per cent. of the theoretical (nearly 40 per cent. being converted into the hydroxy-acid), the action of pyridine as an agent for eliminating hydrogen bromide was investigated, and excellent results were obtained. The bromo-acid dissolves readily in pyridine, and if, after boiling for 5 minutes, the excess of pyridine is removed by evaporation and the residue decomposed by dilute sulphuric acid, a white, crystalline deposit of nearly pure tetrahydro-acid is obtained at once, the yield being almost quantitative. After recrystallising from dilute acetic acid, a sample of the acid prepared in this way was analysed with the following result:

0.1390 gave 0.3489  $\text{CO}_2$  and 0.1082  $\text{H}_2\text{O}$ .  $\text{C} = 68.5$ ;  $\text{H} = 8.7$ .

$\text{C}_8\text{H}_{14}\text{O}_2$  requires  $\text{C} = 68.6$ ;  $\text{H} = 8.6$  per cent.

*Ethyl  $\Delta^3$ -Tetrahydro-*p*-toluate.*—This ester could not be prepared from the acid by treatment with alcohol and hydrogen chloride in the ordinary way, owing to the great ease with which it unites with hydrogen chloride; it was, however, obtained pure in the following manner. The pure acid (25 grams) was digested for three hours on the water-bath with 100 c.c. of a mixture of 1 volume of sulphuric acid and 10 volumes of alcohol, and, after remaining overnight, water was added and the oily ester extracted with ether. The ethereal solution was washed well with water and dilute sodium carbonate, dried over calcium chloride, and evaporated, the residual oil being fractionated under 100 mm. pressure.

Almost the whole distilled at 155—157° as a colourless oil having a pungent and unpleasant odour.

0.1109 gave 0.2893 CO<sub>2</sub> and 0.0949 H<sub>2</sub>O. C = 71.0; H = 9.5.

C<sub>10</sub>H<sub>16</sub>O<sub>2</sub> requires C = 71.4; H = 9.5 per cent.

*γδ-Dibromohexahydro-p-toluic Acid*.—Tetrahydro-*p*-toluic acid shows all the properties of an unsaturated acid, since its solution in sodium carbonate rapidly decolorises permanganate, and the powdered acid is at once attacked by bromine with considerable development of heat and evolution of some hydrogen bromide. In order to prepare the dibromo-additive product, the acid was dissolved in dry chloroform, the solution cooled to -10°, and bromine added drop by drop until the colour just remained permanent. The solution was then exposed in a shallow basin and, when the chloroform had evaporated, a solid residue was obtained which crystallised from formic acid (sp. gr. 1.22) in satiny plates.

0.1396 gave 0.1754 AgBr. Br = 53.4.

C<sub>8</sub>H<sub>12</sub>O<sub>2</sub>Br<sub>2</sub> requires Br = 53.3 per cent.

*γδ-Dibromohexahydro-p-toluic acid* melts at about 104°, but it softens a few degrees below this temperature. It dissolves readily in sodium carbonate, and the solution is stable to permanganate in the cold and, even on warming, reduction takes place only gradually.

*Conversion of Δ<sup>3</sup>-Tetrahydro-p-toluic Acid into p-Toluic Acid by Oxidation with Sulphuric Acid*.—In carrying out this oxidation, the tetrahydro-acid (1 gram) dissolved in concentrated sulphuric acid (10 grams) was heated on the water-bath until the evolution of sulphur dioxide was complete, which was the case after about 10 minutes. The dark brown liquid was diluted with water, the solid mass which separated was collected, washed with water, dried on porous porcelain, and distilled. The distillate was then recrystallised from dilute acetic acid, and the colourless mass of crystals dried at 100°.

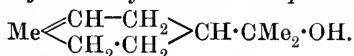
0.1385 gave 0.3575 CO<sub>2</sub> and 0.0748 H<sub>2</sub>O. C = 70.4; H = 6.0.

C<sub>8</sub>H<sub>8</sub>O<sub>2</sub> requires C = 70.6; H = 5.9 per cent.

This acid melted sharply at 179°, and consisted of pure *p*-toluic acid.

*Action of Magnesium Methyl Iodide on Ethyl Δ<sup>3</sup>-Tetrahydro-p-toluate.*

*Synthesis of Inactive Terpeneol.*



In carrying out this synthesis, magnesium (21 grams) was covered with pure dry ether (500 c.c.) and then gradually treated with an

excess of methyl iodide (120 grams),\* the vigorous reaction being kept under control by cooling in running water. As soon as the magnesium had dissolved, ethyl tetrahydro-*p*-toluate (30 grams) was added in one portion, since the reaction takes place apparently only gradually, and with evolution of very little heat. After 24 hours, the product was cautiously decomposed by adding water and dilute hydrochloric acid, the ethereal solution was separated, washed with dilute hydrochloric acid, and evaporated. In order to remove any unchanged ester which might have escaped the action of the magnesium methyl iodide, the yellow, oily residue was mixed with a solution of caustic potash (10 grams) in methyl alcohol and heated on the water-bath for 15 minutes; water was then added and the oil again extracted with ether.

The ethereal solution was carefully freed from methyl alcohol by washing with water, dried over anhydrous sodium sulphate, and the residue, after evaporation, distilled under 60 mm. pressure.

With the exception of a small quantity of a more volatile fraction which had the odour of dipentene, almost the whole quantity distilled at 134—135° as a viscid, colourless oil† which proved to be *inactive terpeneol*. After a second fractionation, the following analytical results were obtained:

0.1592 gave 0.4536 CO<sub>2</sub> and 0.1670 H<sub>2</sub>O. C=77.7; H=11.7.

0.1431 „ 0.4086 CO<sub>2</sub> „ 0.1529 H<sub>2</sub>O. C=77.8; H=11.9.

C<sub>10</sub>H<sub>18</sub>O requires C=77.9; H=11.7 per cent.

That the boiling point given above is that of *terpeneol* was proved by distilling a specimen of pure *terpeneol* in the same apparatus and under the same conditions, when a boiling point identical with that given above was observed. Furthermore, the synthetical substance possessed in a marked degree the odour of lilac, which is so characteristic of *terpeneol*. In order, however, that there should be no doubt as to the identity of the synthetical substance, it was converted into the crystalline nitrosochloride and phenylurethane, which were then compared, and found to be identical with specimens prepared from ordinary *terpeneol*.

*Terpeneolnitrosochloride*, C<sub>10</sub>H<sub>15</sub>O, NOCl.

This derivative was obtained by mixing synthetical *terpeneol* (1.5 grams) with glacial acetic acid (1.5 c.c.) and *isoamyl nitrite* (1.5 c.c.);

\* See footnote, p. 660.

† When this oil was cooled in a freezing mixture, it became very viscid, but did not crystallise even on rubbing with a glass rod, and the same behaviour was noticed in the case of a carefully fractionated sample of liquid *terpeneol*. Subsequently, a specimen of solid *terpeneol* was obtained from Schimmel & Co., and, on adding a minute crystal of this to the synthetical *terpeneol* and cooling in ice, the whole became quite solid.

hydrochloric acid (0.7 c.c.) was then added drop by drop, the whole being carefully cooled in ice and salt during the operation. After 2 hours, the pale green liquid was poured on to powdered ice, when an oil separated which gradually solidified.

In contact with porous porcelain, traces of oily mother liquor were rapidly absorbed, and the residue, after recrystallisation from ethyl acetate, melted at about 119—122°, whereas a specimen of the nitrosochloride, prepared from crystallised terpineol in the same way, melted at 121—123°. The identity was further proved by the fact that the mixture of the two specimens melted at 120—122°.

The specimen from synthetical terpineol was analysed with the following result:

0.1129 gave 0.0724 AgCl. Cl = 15.9.

$C_{10}H_{18}O_2NCl$  requires Cl = 16.1 per cent.

*Terpineolphenylurethane*,  $C_{10}H_{17}O \cdot CO \cdot NH \cdot C_6H_5$ .

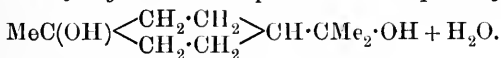
In preparing this substance, synthetical terpineol (1.5 grams) was mixed with phenylcarbimide (1.2 grams), and the whole heated at 60° for one hour and then at 90° for half an hour. On pouring the product on to a watch glass, it soon solidified completely, and was easily purified by recrystallisation from dilute methyl alcohol, from which it separated in colourless needles melting at 113° (compare Wallach, *Annalen*, 1893, 275, 104).

0.1406 gave 6.2 c.c. of nitrogen at 16° and 760 mm. N = 5.2.

$C_{17}H_{23}O_2N$  requires N = 5.1 per cent.

A quantity of the phenylurethane was prepared from crystallised terpineol, and found to melt at the same temperature; moreover, on mixing this with the specimen obtained from synthetical terpineol, no alteration in the melting point could be observed.

*Conversion of Synthetical Terpineol into Terpin Hydrate.*



Tiemann and Schmidt have made the interesting observation (*Ber.*, 1895, 28, 1781) that when terpineol is shaken with dilute sulphuric acid it is slowly converted into terpin hydrate, and as this change is highly characteristic, it was thought important to endeavour to bring it about in the case of the synthetical substance.

Synthetical terpineol (10 grams) was therefore mixed with benzene (5 grams) and shaken in a stoppered bottle, partly by hand and partly on the machine, with 1500 c.c. of 5 per cent. sulphuric acid.

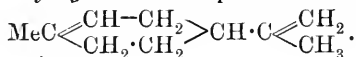
After three days, crystals began to appear on the sides of the bottle, and when the formation of these seemed to be complete (in about 10 days), the whole was filtered and the pasty mass left in contact with porous porcelain until quite dry. The residue, together with a further crop of crystals which were obtained from the sulphuric acid mother liquors by saturating with ammonium sulphate, was then slowly recrystallised from water, and in this way magnificent crystals of *terpin hydrate* were obtained, which, after remaining exposed to the air for 2 days, were analysed.

0.1545 gave 0.3578  $\text{CO}_2$  and 0.1607  $\text{H}_2\text{O}$ .  $\text{C} = 63.1$ ;  $\text{H} = 11.6$ .

$\text{C}_{10}\text{H}_{22}\text{O}_3$  requires  $\text{C} = 63.2$ ;  $\text{H} = 11.6$  per cent.

When rapidly heated, this substance melted at  $120^\circ$  with vigorous decomposition,\* due to evolution of steam, and, when kept in a water oven at  $90^\circ$ , the glistening crystals gradually became opaque and partially sublimed, and the *anhydrous terpin* thus obtained melted at  $105^\circ$ , which is the melting point of ordinary terpin (Wallach, *Annalen*, 1885, 230, 248). Furthermore, an intimate mixture of synthetical and ordinary terpin hydrate melted at exactly the same point as the components, so that there can be no doubt that the synthetical substance is identical in all respects with ordinary terpin hydrate.

*Conversion of Synthetical Terpeneol into Dipentene,*



It is well known that when ordinary terpeneol is heated with potassium hydrogen sulphate it is readily converted, with loss of water, into dipentene, and in order to accomplish this important transformation in the case of synthetical terpeneol, the following experiment was carried out. Synthetical terpeneol (21 grams) was mixed with powdered potassium hydrogen sulphate (30 grams) and heated to boiling for 1 hour in a reflux apparatus, during which it was noticed that much water was produced. After distilling in steam, the oil was extracted with ether, dried over calcium chloride, and roughly fractionated, and the portion boiling above  $185^\circ$ , which contained unchanged terpeneol, again heated with potassium hydrogen sulphate. The dipentene obtained from both experiments was carefully fractionated, and 15 grams were obtained, which distilled at  $180-183^\circ$ , and possessed in a marked degree the characteristic odour of lemons; but this did not

\* This decomposition point is usually given as  $116-117^\circ$ , but if capillary tubes containing terpin hydrate are plunged into sulphuric acid heated in different experiments at temperatures between  $116^\circ$  and  $122^\circ$ , it will be seen that the correct point of decomposition is about  $120-121^\circ$ .

give satisfactory results on analysis. Experiments with ordinary dipentene clearly showed that it is a matter of considerable difficulty to prepare a specimen of dipentene in so pure a condition that it will give good results on analysis, and this is partly due to the rapidity with which this terpene absorbs oxygen from the air. The desired result was, however, ultimately accomplished in the case of the synthetical product by repeated distillation over sodium in a current of dry carbon dioxide, and the sample analysed distilled constantly at  $180-181^{\circ}$ .

0.1351 gave 0.3365  $\text{CO}_2$  and 0.1451  $\text{H}_2\text{O}$ .  $\text{C} = 88.1$ ;  $\text{H} = 11.9$ .

$\text{C}_{10}\text{H}_{16}$  requires  $\text{C} = 88.2$ ;  $\text{H} = 11.8$  per cent.

In order to demonstrate clearly the identity of this synthetical hydrocarbon with ordinary dipentene, the following derivatives were prepared from it, and directly compared with specimens made under exactly the same conditions from pure dipentene.

*Dipentene Dihydrochloride*,  $\text{C}_{10}\text{H}_{16} \cdot 2\text{HCl}$ .—Synthetical dipentene (2 grams) was mixed with glacial acetic acid (1 gram) in a beaker, and gaseous hydrogen chloride led over the surface for about an hour. On mixing the solution with ice and water, an oil separated which readily solidified, and after remaining in contact with porous porcelain until quite dry, the substance was further purified by dissolving in alcohol and precipitating with water as recommended by Wallach (*Annalen*, 1887, 239, 12).

0.1282 gave 0.1767  $\text{AgCl}$ .  $\text{Cl} = 34.1$ .

$\text{C}_{10}\text{H}_{18}\text{Cl}_2$  requires  $\text{Cl} = 34.0$  per cent.

This dihydrochloride melted at  $48-50^{\circ}$ , and was identical in all respects with a specimen prepared from ordinary dipentene.

*Dipentenetetrabromide*,  $\text{C}_{10}\text{H}_{16}\text{Br}_4$ .—This substance was readily obtained by dissolving synthetical dipentene in twice its volume of pure, dry chloroform, cooling to  $-10^{\circ}$ , and adding bromine drop by drop until the yellow colour persisted for 5 minutes.

The solution was freed from chloroform by aspirating a rapid current of dry air over it, and the crystalline residue was dried on porous porcelain and recrystallised from ethyl acetate, when it separated in colourless, glistening needles.

0.1344 gave 0.2213  $\text{AgBr}$ .  $\text{Br} = 70.1$ .

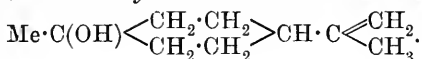
$\text{C}_{10}\text{H}_{16}\text{Br}_4$  requires  $\text{Br} = 70.2$  per cent.

Thus prepared, the tetrabromide melted at  $125^{\circ}$ , and when mixed with an equal quantity of ordinary dipentenetetrabromide, no alteration in the melting point could be detected.

*Dipentenitrosochloride*,  $\text{C}_{10}\text{H}_{16}\text{NOCl}$ .—This substance was prepared from synthetical dipentene by the method recommended by

Wallach (*Annalen*, 1888, 245, 268); it melted at 106°, and was identical in all respects with ordinary dipentenitrosochloride.

*Hydroxyisopropyl-p-ketohexamethylene, isoPropenyl-p-ketohexamethylene, and the Conversion of the latter into  $\Delta^{8(9)}$ -Menthenol (1),*



In describing the action of magnesium methyl iodide on ethyl  $\delta$ -ketohexahydrobenzoate (p. 660), it was mentioned that a neutral oil, unaffected by the treatment with methyl-alcoholic potash, and having an intense odour of peppermint, is always produced in small quantity.

During the course of this research, about 30 grams of this oil were gradually accumulated and then treated as follows.

It was first distilled in steam and then repeatedly fractionated under 100 mm. pressure, and thus separated into two portions boiling at 135—150° and 177—180°. The latter, which was about two-thirds of the whole, was analysed with the following result:

0.1113 gave 0.2799 CO<sub>2</sub> and 0.1048 H<sub>2</sub>O. C = 68.6; H = 10.4.  
CO(CH<sub>2</sub>·CH<sub>2</sub>)<sub>2</sub>CH·CMe<sub>2</sub>·OH or C<sub>9</sub>H<sub>16</sub>O<sub>2</sub> requires C = 69.2; H = 10.2 per cent.

As explained in the introduction (p. 659), this analysis and the method of formation of the substance leave scarcely any doubt that it is hydroxyisopropyl-*p*-ketohexamethylene. It is a viscid oil which is readily volatile in steam.

The lower fraction, boiling at 135—150° (100 mm.), was repeatedly distilled under the ordinary pressure, and about 10 grams were thus isolated, which boiled, not quite constantly, at 184—186°.

0.1507 gave 0.4286 CO<sub>2</sub> and 0.1369 H<sub>2</sub>O. C = 77.3; H = 10.1.  
CO(CH<sub>2</sub>·CH<sub>2</sub>)<sub>2</sub>CH·CMe·CH<sub>2</sub> or C<sub>9</sub>H<sub>14</sub>O requires C = 78.2; H = 10.1 per cent.

This substance evidently has the composition C<sub>9</sub>H<sub>14</sub>O, and is derived from hydroxyisopropylketohexamethylene by the elimination of water, but as it could not be completely separated from this hydroxy-compound by fractionation, it was shaken with aqueous hydrobromic acid (saturated at 0°), and the heavy bromide thus produced digested with methyl-alcoholic potash. After extracting in the usual way, the resulting oil distilled at the same temperature as before, and gave on analysis numbers agreeing rather more closely with the formula C<sub>9</sub>H<sub>14</sub>O.

0.1211 gave 0.3449  $\text{CO}_2$  and 0.1110  $\text{H}_2\text{O}$ .  $\text{C} = 77.6$ ;  $\text{H} = 10.2$ .

$\text{C}_9\text{H}_{14}\text{O}$  requires  $\text{C} = 78.2$ ;  $\text{H} = 10.1$  per cent.

This *isopropenyl-p-ketohecamethylene* is isomeric with phorone, acetophorone, camphorone, and many other similar ketones, and with these it shares the property of possessing a penetrating odour of peppermint. The conversion of this ketone into  $\Delta^{8(9)}$ -menthenol (1), which is discussed in the introduction (p. 659), was carried out as follows. Magnesium (3 grams) was covered with dry ether (100 c.c.) and converted into magnesium methyl iodide by treatment with 25 grams of methyl iodide; the ketone (6 grams), dissolved in ether (20 c.c.), was then added, and the whole left for 24 hours. The product was then decomposed by dilute hydrochloric acid, the ethereal solution separated, washed with water, evaporated, and the residual oil, after distilling in steam, fractionated under 60 mm. pressure. Almost the whole quantity distilled at  $125-127^\circ$ , or about  $8^\circ$  lower than terpineol, with which it is isomeric, and there can be no doubt that this synthetical substance is identical with the  $\Delta^{8(9)}$ -menthenol (1) of Stephan and Helle (*Ber.*, 1902, 35, 2147), and which melts at  $32^\circ$ .

0.1506 gave 0.4298  $\text{CO}_2$  and 0.1625  $\text{H}_2\text{O}$ .  $\text{C} = 77.9$ ;  $\text{H} = 11.9$ .

$\text{C}_{10}\text{H}_{18}\text{O}$  requires  $\text{C} = 77.9$ ;  $\text{H} = 11.7$  per cent.

The viscid oil thus obtained had a very pronounced odour of hyacinths, and when cooled in ice and well stirred, it crystallised; but owing to the small amount of material available no attempt could be made to recrystallise it and determine its melting point.

On treatment with *isoamyl* nitrite and hydrochloric acid in acetic acid solution, it yielded a crystalline nitrosochloride, and phenylcarbimide converted it into a phenylurethane, which, after crystallisation from dilute methyl alcohol, melted at  $85-87^\circ$ , whereas Stephan and Helle give  $85^\circ$  as the melting point of the phenylurethane of  $\Delta^{8(9)}$ -menthenol (1).

The author wishes to express his thanks to Mr. S. S. Pickles, B.Sc., for his valuable assistance in carrying out this difficult investigation, and to state that much of the expense incurred has been met by repeated grants from the Government Grant Fund of the Royal Society.

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LXVII.—*Ammoniacal Double Chromates and Molybdates.*

By SAMUEL HENRY CLIFFORD BRIGGS.

In a previous paper (Trans., 1903, 83, 391), a number of double chromates were described belonging to a series having the general formula  $M_2^I M^{II} (RO_4)_2, 2NH_3$ .

Since the majority of the comparatively small number of ammoniacal double salts which have been prepared are halides or cyanides, it seemed worth while to make a more complete examination of this series, and compounds have been obtained in which  $M^I$  represents  $NH_4$  or K;  $M^{II}$  is Cu, Zn, Cd, Ni, or Co; and R is Cr or Mo. Numerous attempts to prepare the corresponding tungstates were unsuccessful.

The double salts are characterised by considerable stability. They may be heated at  $150^\circ$  without undergoing any change, and in some cases ammonia is not given off at temperatures above  $200^\circ$ . Decomposition always occurs below  $300^\circ$ , the ammonia being partially oxidised at the expense of the acid radicle.

The stability of the double salts is in marked contrast to the readiness with which ammonia is evolved from many ammonio-metallic compounds, such as  $CuCrO_4, 3\frac{1}{2}NH_3, \frac{1}{2}H_2O$ ,  $CuMoO_4, 2NH_3, H_2O$ , and  $CuWO_4, 4NH_3$ , which are described in the present paper. A further distinction between the two classes of substances is presented in their respective colours. The double salt  $(NH_4)_2Cu(MoO_4)_2, 2NH_3$  is bright blue, similar in tint to hydrated copper sulphate, whereas the compound  $CuMoO_4, 2NH_3, H_2O$  has the deep blue shade usually associated with cuprammonium compounds. Again, although ammonio-nickel compounds are generally blue or violet, the double salt  $(NH_4)_2Ni(MoO_4)_2, 2NH_3$  is green.

*Chromates.*

*Ammonio-copper potassium chromate*,  $K_2Cu(CrO_4)_2, 2NH_3$ , crystallises out when an ammoniacal solution of copper chromate to which a large amount (3 to 4 equivalents) of potassium chromate has been added is allowed to lose its free ammonia by exposure to the air.

Copper carbonate (12.5 grams) was dissolved in a small quantity of water containing 25 grams of chromium trioxide, and the solution added to a mixture of 75 c.c. of water and 125 c.c. of concentrated aqueous ammonia. A second solution containing 20 grams of potassium hydroxide and 150 grams of potassium chromate in 280 c.c. of water was then added, and the liquid filtered. The function of the potassium hydroxide was to diminish the concentration of the

ammonium ions, and thus prevent as far as possible the formation of an isomorphous mixture of potassium and ammonium salts.

After the filtrate had remained for a few days in an open dish, the compound separated in large, hard rosettes of thin, brown plates closely set together. These were broken up, washed by decantation with the mother liquor to remove any basic salt, then with dilute ammonia, and finally dried with alcohol and ether.

	Found.	Required.
CuO .....	19.34	19.44 per cent.
CrO <sub>3</sub> .....	49.06	49.16 „
NH <sub>3</sub> .....	8.8	8.4 „

The compound was decomposed by water and dissolved readily in dilute ammonia. When heated at 250° it gave off a little ammonia and decomposed rapidly at 280°.

*Ammonio-copper chromate*,  $\text{CuCrO}_4 \cdot 3\frac{1}{2}\text{NH}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ , was obtained from the same solution in large, greenish-black crystals, when the potassium chromate present was insufficient for the formation of the double salt  $\text{K}_2\text{Cu}(\text{CrO}_4)_2 \cdot 2\text{NH}_3$ . Its preparation was accomplished by dissolving 14 grams of copper carbonate and 25 grams of chromium trioxide in a small amount of water, pouring the solution into a mixture containing 125 c.c. of concentrated ammonia, 50 c.c. of water, and 15 grams of potassium hydroxide, and exposing the filtered liquid to the air.

	Found.		Required.
	I.	II.	
CuO .....	31.95	32.23	32.01 per cent.
CrO <sub>3</sub> .....	40.16	40.10	40.30 „
NH <sub>3</sub> .....	23.86	23.72	24.01 „

The crystals, which readily evolve ammonia at the ordinary temperature, are easily soluble in dilute ammonia, but are decomposed by water. Although several ammoniacal copper chromates have been previously described, this is the first one known containing the acidic and basic oxides in equivalent proportion (1 : 1).

### *Molybdates.*

The double salts of ammonium molybdate belonging to this series, like the chromates, are well-defined, crystalline substances, readily obtained in a state of purity; they are decomposed by water but dissolve easily in dilute ammonia, in which they appear to be resolved to some extent into their components.

*Ammonio-copper ammonium molybdate*,  $(\text{NH}_4)_2\text{Cu}(\text{MoO}_4)_2 \cdot 2\text{NH}_3$ .—Fifty grams of ammonium molybdate in 60 c.c. of water were added

to a solution of 20 grams of ordinary copper sulphate in 50 c.c. of water and 70 c.c. of concentrated ammonia, the liquid being then made up to 210 c.c. After leaving the solution in an open dish for five days, the large, bright blue crystals were collected, washed with dilute ammonia, and dried with alcohol and ether.

	Found.	Required.
CuO .....	17.46	17.49 per cent.
MoO <sub>3</sub> .....	63.58	63.52 „
NH <sub>3</sub> .....	15.12	15.02 „

*Ammonio-copper molybdate*,  $\text{CuMoO}_4 \cdot 2\text{NH}_3 \cdot \text{H}_2\text{O}$ , crystallises in deep blue prisms on exposing to the air an ammoniacal solution of copper sulphate and ammonium molybdate which contains too small an amount of molybdate or is too dilute for the formation of the double salt. For its preparation, 24 grams of copper sulphate in 30 c.c. of water were added to 13 grams of ammonium molybdate in 15 c.c. of water and 40 c.c. of strong ammonia, the whole solution being made up to 350 c.c.

	Found.		Required.
	I.	II.	
CuO.....	28.75	28.74	28.87 per cent.
MoO <sub>3</sub> .....	52.66	52.53	52.29 „
NH <sub>3</sub> .....	—	12.53	12.37 „

The habit of the crystals varies greatly with the proportion of copper sulphate and ammonium molybdate present in the solution, an excess of the latter being accompanied by a large development of certain faces which remain insignificant when a considerable amount of the former is used. The compound evolves ammonia at the ordinary temperature; it is soluble in dilute ammonia, from which it may be re-crystallised either by allowing a warm saturated solution to cool, or by exposing a more dilute solution to the air.

*Ammonio-cadmium ammonium molybdate*,  $(\text{NH}_4)_2\text{Cd}(\text{MoO}_4)_2 \cdot 2\text{NH}_3$ , was prepared in the same way as the corresponding copper compound.

	Found.	Required.
CdO .....	25.69	25.49 per cent.
MoO <sub>3</sub> .....	57.72	57.36 „
NH <sub>3</sub> .....	13.47	13.56 „

When heated quickly, the colourless crystals evolved ammonia and water giving 78.6 per cent. of a black residue, whereas  $2\text{CdMoO}_4 \cdot \text{Mo}_2\text{O}_3$  requires 78.1 per cent. The black residue containing molybdenum sesquioxide on further heating in the air was oxidised, becoming white (residue found = 81.3;  $\text{CdMoO}_4 \cdot \text{MoO}_3$  requires 82.8 per cent.). This decomposition is similar to, but not so complete as, that of the salt

$(\text{NH}_4)_2\text{Cd}(\text{CrO}_4)_2, 2\text{NH}_3$ , which on heating gave  $\text{CdO}, \text{Cr}_2\text{O}_3$  (*loc. cit.*). At a higher temperature a molecule of molybdic anhydride sublimed, leaving cadmium molybdate (found  $\text{CdMoO}_4 = 54.4$ , required  $54.2$  per cent.).

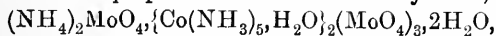
*Ammonio-nickel ammonium molybdate*,  $(\text{NH}_4)_2\text{Ni}(\text{MoO}_4)_2, 2\text{NH}_3$ .—Twenty grams of hexahydrated nickel chloride dissolved in 15 c.c. of water were added to 50 grams of ammonium molybdate in 70 c.c. of strong ammonia and 50 c.c. of water. The deep blue liquid when left in an open dish deposited green crystals of the double salt.

	Found.	Required.
NiO .....	16.79	16.70 per cent.
MoO <sub>3</sub> .....	64.24	64.14 „
NH <sub>3</sub> .....	15.00	15.18 „

*Ammonio-cobalt ammonium molybdate*,  $(\text{NH}_4)_2\text{Co}(\text{MoO}_4)_2, 2\text{NH}_3$ .—A solution made up from 20 grams of cobalt sulphate, 50 grams of ammonium molybdate, 50 c.c. of strong ammonia, and 90 c.c. of water oxidised rapidly in the air; and consequently in order to obtain the cobaltous double salt it was placed over sulphuric acid in a vacuum desiccator connected with a water-pump, which was kept in action until the excess of ammonia had been evolved. The double salt was deposited in small, violet crystals, which were collected, washed with dilute ammonia, and dried with alcohol and ether.

	Found.	Required.
CoO.....	17.03	16.70 per cent.
MoO <sub>3</sub> .....	64.30	64.14 „
NH <sub>3</sub> .....	14.8	15.2 „

If the solution was allowed to oxidise in the air, it deposited a large quantity of brilliant crimson needles, which dissolved in dilute ammonia, but were slightly decomposed by water; they were easily soluble in potassium hydroxide, and the solution on boiling evolved ammonia, the cobalt being precipitated. An analysis gave  $\text{CoO} = 14.85$ ,  $\text{MoO}_3 = 55.65$  and  $55.72$ ,  $\text{NH}_3 = 19.66$ , these figures corresponding with ammonium aquopentamminocobaltic molybdate,



which requires  $\text{CoO} = 14.47$ ,  $\text{MoO}_3 = 55.57$ , and  $\text{NH}_3 = 19.73$  per cent., but the examination of the compound was not sufficiently complete to justify any conclusions with regard to its constitution.

### *Tungstates.*

The following new substances were obtained during the unsuccessful experiments made with the object of preparing ammoniacal double tungstates.

The copper compound  $\text{CuO}, 4\text{WO}_3, 6\text{NH}_3, 8\text{H}_2\text{O}$  separated as a dirty-blue, microcrystalline mass when an ammoniacal solution of copper sulphate and ammonium tungstate gave off its excess of ammonia. If the evolution of ammonia was very slow, the compound was obtained in small, bright blue needles.

Tungstic acid corresponding with 20 grams of tungstic anhydride, obtained by precipitating a solution of sodium tungstate,  $\text{Na}_2\text{WO}_4$ , with nitric acid, was dissolved in 20 c.c. of cold concentrated ammonia, 5 grams of copper sulphate in 7.5 c.c. of water and 7.5 c.c. of concentrated ammonia were added, and the filtered solution placed in an open vessel. The large crystals were used for analysis.

	Found.	Required.
$\text{CuO}$ .....	6.43	6.35 per cent.
$\text{WO}_3$ .....	73.93	74.01 „
$\text{NH}_3$ .....	8.18	8.15 „
$\text{H}_2\text{O}$ .....	11.46 (by difference)	11.48 „

The crystals were almost insoluble in dilute ammonia and insoluble in water.

*Ammonio-copper Tungstate,  $\text{CuWO}_4, 4\text{NH}_3$ .*

(1) Copper sulphate (7.5 grams) was precipitated in hot solution with 10 grams of dihydrated sodium tungstate,  $\text{Na}_2\text{WO}_4, 2\text{H}_2\text{O}$ , the precipitated copper tungstate washed by decantation and thoroughly drained, after which it was dissolved in 20 c.c. of cold concentrated ammonia.

(2) Dihydrated sodium tungstate (13 grams) was precipitated with nitric acid, and the washed tungstic acid, after being drained, was dissolved in 20 c.c. of strong ammonia, the solution being added to the ammoniacal solution of copper tungstate. The mixture was then filtered into a bottle, and a layer of alcohol allowed to diffuse slowly into it during several weeks, the bottle remaining tightly stoppered. The experiment was arranged in this way with the object of preventing the ammonia from being given off to such an extent as would result in the formation of polytungstates. This end was achieved, only the normal tungstate being obtained, but no double salt was observed even when three times as much ammonium tungstate was present as in the experiment under consideration. The compound  $\text{CuWO}_4, 4\text{NH}_3$  separated in both cases.

	Found.	Required.
$\text{CuO}$ .....	20.80	20.96 per cent.
$\text{WO}_3$ .....	61.16	61.09 „
$\text{NH}_3$ .....	18.15	17.95 „

The deep blue crystals, which dissolved in a small amount of water and were easily soluble in dilute ammonia, gave off ammonia very readily at the ordinary temperature.

*Ammonio-zinc tungstate*,  $\text{ZnWO}_4 \cdot 4\text{NH}_3 \cdot 3\text{H}_2\text{O}$ , crystallised in large, transparent tetrahedra often exhibiting twinning; it readily evolved ammonia at the ordinary temperature.

	Found.	Required.
ZnO .....	18.49	18.66 per cent.
WO <sub>3</sub> .....	54.0	53.3   ,,
NH <sub>3</sub> .....	15.61	15.65   ,,

It was prepared like the foregoing copper salt, the zinc tungstate being precipitated in the cold, since that which comes down from hot solutions is not easily soluble in ammonia.

### LXVIII.—*The Hexahydrated Double Chromates. Magnesium and Nickel Compounds.*

By SAMUEL HENRY CLIFFORD BRIGGS.

THE double chromates  $\text{M}_2\text{M}^{\text{II}}(\text{CrO}_4)_2 \cdot 6\text{H}_2\text{O}$ , which are of some interest on account of their analogy with the corresponding double sulphates, have been but slightly investigated, only two members of the series having been hitherto prepared, namely, magnesium ammonium chromate,  $(\text{NH}_4)_2\text{Mg}(\text{CrO}_4)_2 \cdot 6\text{H}_2\text{O}$  (Grailich, *Sitzungsber. Akad. Wissen. Wien.*, 1857, 27, 175), and nickel ammonium chromate (Briggs, *Trans.*, 1903, 83, 391).

The continuation of the experiments described in the previous paper (*loc. cit.*) has led to the isolation of nickel potassium chromate,  $\text{K}_2\text{Ni}(\text{CrO}_4)_2 \cdot 6\text{H}_2\text{O}$ , a compound which is very efflorescent at the ordinary temperature.

It was shown by Tutton (*Trans.*, 1896, 69, 521) that, in the case of the double sulphates the stability of those compounds which contain the same bivalent metal increases with the increase in the atomic weight of the alkali metal. Thus the double salt  $\text{K}_2\text{Cd}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  could not be prepared,  $\text{Rb}_2\text{Cd}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  was very efflorescent, and  $\text{Cs}_2\text{Cd}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  much less so at the ordinary temperature. Consequently, it seemed probable that a similar increase in stability from the potassium to the caesium compounds would hold good for the double chromates, and for this reason the rubidium and caesium salts were examined, with the result that the latter was found to be quite stable at 10°, whereas the former became slightly discoloured after

being kept for two months. Nickel ammonium chromate occupies an intermediate position between the two in agreement with the place in the alkali series assigned to ammonium by Tutton in a recent paper on the morphological and physical properties of ammonium sulphate (Trans., 1903, 83, 1049).

The double salts of magnesium chromate have also been prepared, and the same differences in stability observed. From the readiness with which magnesium potassium chromate and nickel potassium chromate give off their water at the ordinary temperature, it seems likely that all the potassium compounds of this group would be efflorescent if they could be obtained, since Tutton (Trans., 1896, 69, 521) found that nickel potassium sulphate was one of the most stable potassium double sulphates which he examined.

#### EXPERIMENTAL.

##### *Nickel Potassium Chromate*, $K_2Ni(CrO_4)_2 \cdot 6H_2O$ .

Eight grams of potassium chromate in 14 c.c. of water were added to 8 grams of nickel acetate in 27 c.c. of water, both solutions having been previously cooled to  $-6^\circ$  in a mixture of ice and salt. If the temperature rises much above this, basic salts separate, these substances also being deposited if the solution is left for any length of time in the freezing mixture. In order to obtain a good yield, it is therefore necessary to induce crystallisation by vigorous stirring. Working in this way, 3.2 grams of the double salt were prepared in the form of small, yellowish-green crystals; these were collected at the pump, washed with a very small quantity of cold water, and dried with alcohol and ether.

Two different preparations gave the following analytical results :

	Found.		Required.
	I.	II.	
$CrO_3$ .....	41.5	41.3	41.95 per cent.
$NiO$ .....	16.0	15.9	15.65 „

The compound, when kept in a stoppered bottle at  $10^\circ$  for a few hours, evolved water and was converted into a damp, brownish-yellow mass. After exposing a portion of each preparation to the air until the weight was constant, the residues contained 47.67 and 47.81 per cent. of chromium trioxide respectively; a loss of three molecules of water requires 47.30 per cent.

*Nickel Rubidium Chromate*,  $Rb_2Ni(CrO_4)_2 \cdot 6H_2O$ .—This double salt separated readily when a solution of rubidium chromate (5 grams in 7 c.c. of water) was added to a solution of nickel acetate (4.3 grams

in 13 c.c. of water) at 10°. The yellowish-green crystals (3·5 grams) were washed with water and dried with alcohol and ether.

	Found.	Required.
NiO .....	13·28	13·12 per cent.
CrO <sub>3</sub> .....	34·85	35·14 „

Nickel rubidium chromate is very slightly efflorescent at the ordinary temperature.

*Nickel caesium chromate*,  $\text{Cs}_2\text{Ni}(\text{CrO}_4)_2 \cdot 6\text{H}_2\text{O}$ , was prepared in the same way as the rubidium compound, 3·8 grams being obtained from 5 grams of caesium chromate and 3 grams of nickel acetate.

	Found.	Required.
NiO .....	11·30	11·26 per cent.
CrO <sub>3</sub> .....	30·25	30·11 „

The crystals were unaltered after having been kept for two months. The salt dissolves in cold water without much change, but is decomposed by warm water; nevertheless, it may be partially recrystallised from a solution saturated at 35—40°, after filtering off the precipitate of basic salt. The potassium compound is much more readily decomposed by water.

*Magnesium Potassium Chromate*,  $\text{K}_2\text{Mg}(\text{CrO}_4)_2 \cdot 6\text{H}_2\text{O}$ .—Dammer states (*Handbuch Anorg. Chem.*), on the authority of v. Hauer (*Sitzungsber. Akad. Wissen. Wien.*, 1860, 39, 440), that magnesium potassium chromate never crystallises with  $6\text{H}_2\text{O}$ . The hexahydrate appears to be formed, however, in a solution of its components, if the temperature is sufficiently low. For its preparation, very concentrated solutions of potassium chromate and magnesium chromate were cooled to -10°, and then mixed. The double salt was deposited in very small, lemon-yellow crystals, which were dried with alcohol and ether.

	Found.	Required.
MgO .....	9·42	9·12 per cent.
CrO <sub>3</sub> .....	45·36	45·25 „
H <sub>2</sub> O .....	23·93	24·39 „

The compound is efflorescent, and a portion on exposure to the air at 8—10° lost 14·92 per cent. of water, a loss of  $4\text{H}_2\text{O}$  requiring 16·25 per cent. The efflorescence did not appear to take place quite so readily as in the case of the corresponding nickel compound.

*Magnesium rubidium chromate*,  $\text{Rb}_2\text{Mg}(\text{CrO}_4)_2 \cdot 6\text{H}_2\text{O}$ , separated in brilliant lemon-yellow crystals, permanent at the ordinary temperature, when solutions of its components were mixed in the cold.

	Found.	Required.
MgO .....	7.88	7.54 per cent.
CrO <sub>3</sub> .....	37.04	37.39 „
H <sub>2</sub> O .....	20.10	20.17 „

*Magnesium caesium chromate*,  $\text{Cs}_2\text{Mg}(\text{CrO}_4)_2 \cdot 6\text{H}_2\text{O}$ , was prepared like the rubidium compound, which it closely resembled.

	Found.	Required.
MgO .....	6.80	6.40 per cent.
CrO <sub>3</sub> .....	31.64	31.75 „
H <sub>2</sub> O .....	17.26	17.15 „

### *Comparison of Stabilities.*

*Nickel Compounds.*—The potassium salt being efflorescent at the ordinary temperature, only the rubidium, ammonium, and caesium compounds were dealt with in these experiments.

(1) Approximately equal quantities of the caesium and rubidium salts were heated together for 12 hours in an air-bath at 40°, after which the rubidium compound had become slightly brown, having lost 0.5 per cent. of water, whereas the caesium compound was unchanged. After further heating for 1 hour at 60°, the caesium compound was also slightly discoloured. The temperature was therefore lowered to 50° for 4 hours, when the rubidium salt had lost 2.4 molecules of water and the caesium salt only 0.15 molecule.

(2) When the ammonium and rubidium compounds were heated together for 2 hours at 53°, the former lost 0.78 molecule and the latter 2 molecules of water. A repetition of the experiment gave exactly the same result.

(3) The ammonium and caesium salts were heated together for 1 hour at 56°. The ammonium compound lost 0.41 molecule of water, becoming brown, whereas the change in weight of the caesium compound was imperceptible.

The order of increasing stability is evidently potassium, rubidium, ammonium, and caesium; but, as is seen from the above experiments, the difference between the potassium and rubidium compounds is more marked than that between the rubidium and caesium salts.

*Magnesium Compounds.*—The caesium and rubidium salts were heated together for 12 hours at 55°. The caesium salt remained unchanged, whilst the rubidium compound lost only 0.16 per cent. of water. The heating was therefore continued for 3 hours at 65°, after which the caesium compound had lost 0.18 and the rubidium derivative 1.6 molecules of water respectively.

Here again the order of increasing stability coincides with the increase in the atomic weight of the alkali metal, the magnesium compounds being somewhat less readily decomposed than their nickel analogues.

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## LXIX.—*Reduced Silicates.*

By CHARLES SIMMONDS, B.Sc.

IN a recent communication (Trans., 1903, 83, 1449) some experiments were recorded describing the reduction which silicates of lead, copper, iron, cobalt, and nickel undergo when heated in hydrogen. The bearing of the results on the structural formulæ of the silicates was pointed out, but the reduced silicates themselves were only alluded to very briefly. The object of the present note is to describe these products, and particularly those obtained from the simpler lead silicates, somewhat more fully.

The first point to decide was whether the substance left after the reduction of any silicate was a mixture of the metal and silica, or a compound of these two substances. Apparently no such compounds have hitherto been recognised, but in the present experiments it is shown that a substance of this nature is formed in all the cases yet examined. In some instances, however, this compound is found to be mixed with a certain proportion of the metal ; and whether this result is obtained or not depends on the composition of the original silicate.

Firstly, taking those lead silicates which do not yield metallic lead on reduction, it is found that lead metasilicate,  $\text{PbSiO}_3$ , the disilicate,  $\text{PbSi}_2\text{O}_5$ , and the trisilicate,  $\text{Pb}_2\text{Si}_3\text{O}_8$ , yield the compounds  $\text{PbSiO}_2$ ,  $\text{PbSi}_2\text{O}_4$ , and  $\text{Pb}_2\text{Si}_3\text{O}_6$  respectively. The evidence on which the conclusion is based that these are true compounds and not mixtures is as follows :

(1) No globules of metallic lead are observable in the reduced substance ; nor is the porcelain boat, in which the silicate is reduced, discoloured or attacked in any way. The residue is friable, and can be triturated to any degree of fineness without showing particles of lead.

(2) When the residue is fused with alkali carbonates no metallic lead is separated ; or, at most, insignificant traces only.

(3) Boiling nitric acid extracts from the reduced residue a relatively small fraction only of the lead present, and in some cases practically none. The following experiments are typical :

(a) Reduced residue from lead metasilicate. Percentage composi-

tion,  $\text{Pb} = 77.6$ ,  $\text{SiO}_2 = 22.4$ . 0.2 gram boiled for a quarter of an hour with 10 c.c. of nitric acid (sp. gr. 1.2). Lead dissolved = 0.0102 gram, or 5.1 per cent.

(b) A similar experiment with 0.2 gram of the reduced residue obtained from lead trisilicate, and containing 69.6 per cent. of lead.

Lead dissolved = 0.0044 gram, or 2.2 per cent.

These experiments show that the reduced silicates contained little or no metallic lead. Moreover, the reduced compound itself, although containing in one case upwards of 77 per cent. of lead, is not attacked to any considerable extent by boiling nitric acid.

Generally, the results obtained from a number of such experiments showed that long-continued boiling with nitric acid might dissolve from the reduced silicates quantities of lead varying from 2 up to about 10 per cent. But in none of these cases could any evidence be obtained that anything more than an insignificant fraction of the lead dissolved was originally present in the metallic condition.

Similar results were obtained with the complex silicates and borosilicates of lead, aluminium, calcium, and the alkali metals. For example, a specimen of complex boro-metasilicate gave a reduced residue in which lead was present to the extent of 45.7 per cent.; from this, when boiled with nitric acid, mere traces of lead were dissolved. Other specimens gave larger, but still relatively small, amounts of lead, ranging up to about 8 per cent.

It is concluded, therefore, that the reduced silicate residues in the above cases were not mixtures of lead and silica, but true compounds. These compounds may perhaps be conveniently designated "*silicites*," to denote that they contain less oxygen than the silicates from which they were derived.

*General Properties.*—Reduced lead silicates ("*silicites*") are black powders, distinctly less fusible than the original silicates. They are not readily re-oxidised: bromine has little or no action on them; and as a rule the compounds can be heated to redness in air for some hours without any considerable increase of weight or change in colour. Except for a slight solvent action, acid oxidising mixtures do not affect them. In one experiment, for instance, 0.5 gram of a complex lead "*silicite*" was boiled for some time with 50 c.c. of aqua regia, and again with nitric acid and potassium chlorate; the residue after this treatment showed no change in appearance, and only 4 per cent. of it had been dissolved. In their chemical deportment the "*silicites*" are frequently more refractory than the original silicates, for whereas the latter were in several instances found to be readily decomposable with cold dilute acids, the "*silicites*" obtained from them were practically unattacked even by hot acids of much greater concentration. A boiling solution of caustic soda extracts small quantities of lead and silica

from the compounds, but does not affect them to any considerable extent. Fusion with alkali carbonates, however, readily decomposes them, and they are also attacked, although with some difficulty, by hydrofluoric acid.

On the other hand, the residues left by the reduction of lead orthosilicate,  $\text{Pb}_2\text{SiO}_4$ , and of the basic disilicate,  $\text{Pb}_3\text{Si}_2\text{O}_7$ , differ notably from the foregoing, inasmuch as they contain, in each case, both a compound ("silicite") and a considerable proportion of metallic lead. As this fact has an important bearing on the question of the constitution of these silicates, the details of a typical experiment are now given:

0.5 gram of lead orthosilicate ( $\text{PbO} = 88.1$ ;  $\text{SiO}_2 = 11.9$  per cent.) was reduced with hydrogen as described in the previous paper (*loc. cit.*), care being taken to spread the silicate in a thin layer over the boat and to raise the temperature rather slowly, as otherwise there is a danger of a surface-coating of metallic lead being formed and protecting the subjacent portion from the action of the hydrogen. In this experiment the reduction was proved to be complete, both by the quantity of water produced and by the loss of weight shown by the reduced silicate. Visible globules of metallic lead were formed, and a thick film of the metal covered the bottom of the boat. After cooling, the boat with its contents was transferred to a beaker, and boiled with about 70 c.c. of nitric acid (sp. gr. 1.2). The solution contained lead equivalent to 57.2 per cent. of the reduced residue, in which the total lead amounted to 87.3 per cent. The insoluble portion was a black powder; it gave up practically no lead when further treated with nitric acid, and proved to be a compound having the following percentage composition:  $\text{Pb} = 68.4$ ;  $\text{SiO}_2 = 31.6$ .

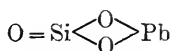
Similar results were given by the basic disilicate,  $\text{Pb}_3\text{Si}_2\text{O}_7$ , except that the proportion of lead dissolved out was relatively larger. Nearly two-thirds of the total amount of lead could be extracted from the residue by boiling with nitric acid. The insoluble portion had, approximately, the percentage composition corresponding with the formula  $\text{Pb}(\text{SiO}_2)_2$ .

The lead silicates, therefore, fall into two groups: (1) those which yield a compound ("silicite") alone on reduction; and (2) those which give a mixture of "silicite" and metallic lead. The first group comprises those silicates in which the number of molecules of basic oxide is not greater than the number of molecules of acidic oxide:  $\text{PbO}, \text{SiO}_2$ ;  $2\text{PbO}, 3\text{SiO}_2$ ;  $\text{PbO}, 2\text{SiO}_2$ ; whereas in the second group the number of molecules of basic oxide is greater than that of the acidic oxide:

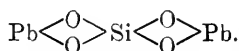
$2\text{PbO}, \text{SiO}_2$   
Orthosilicate.

$3\text{PbO}, 2\text{SiO}_2$ .  
Basic disilicate.

It has been pointed out in the previous communication (*loc. cit.*, p. 1462) that the elimination of metallic lead from the silicates in the second group during reduction, but not from those of the first group, is not readily explained by the ordinary formulæ :

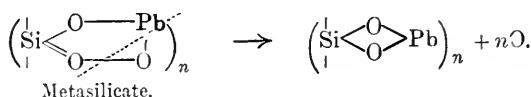


Metasilicate.

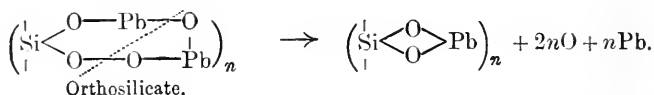


Orthosilicate.

But the elimination becomes explicable when the silicates are formulated on the system which the author has suggested :



Metasilicate.



Orthosilicate.

On this view, one-half of the lead should be eliminated in the metallic state when the orthosilicate is reduced. Treatment of the reduced residue with nitric acid should therefore dissolve out one-half the total quantity of lead, *plus* whatever amount may be dissolved by the simultaneous action of the acid on the residual compound ("silicite.") In the foregoing experiment, the total lead was 87.3 per cent., and the amount dissolved by nitric acid was 57.2 per cent., or 13.5 per cent. more than the amount required by the above expression. Since from some of the lead "silicites" alone (that is, from those containing no metallic lead) quantities of lead up to about 10 per cent. were extracted by nitric acid, it seems reasonable to assume that this quantity, 13.5 per cent., was in like manner derived from the "silicite" portion of the mixture left on reducing the orthosilicate. It was not found practicable to extract the whole of the metallic lead except by using an acid as solvent, because a portion of the metal had become slightly fused to the glaze of the porcelain boat.

Substantially similar results were obtained with various silicates of copper, iron, cobalt, and nickel. The general conclusion deduced confirmed that indicated by the study of the lead silicates, namely, that a compound of the metal and silica is always formed on reducing the silicate, but that in certain cases this compound may be mixed with more or less of the uncombined metal.

The experiments described would therefore appear to afford some evidence in favour of the theory of the structure of silicates which was put forward in the earlier communication. It may also be of interest

to note that, since flint-glass is a compound approximating to the disilicate type, it should, according to the foregoing results, give on reduction a black "silicite," and no metallic lead. Consequently the blackening which occurs when such glass is heated in a reducing flame, and which is usually attributed to the production of metallic lead, is more probably due to the formation of a film of lead "silicite." As a matter of fact, some powdered flint-glass was reduced in hydrogen and tested, but no uncombined lead could be detected in the residue.

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## LXX.—*Studies on Optically Active Carbimides. Part I.*

By ALLEN NEVILLE, B.Sc. (Lond.), and ROBERT HOWSON PICKARD.

ON account of the ease with which carbimides, and particularly aromatic carbimides, react with alcohols and amines, and owing also to the well-defined crystalline nature of the products, an optically active carbimide, if obtainable, would seem to be a promising reagent to employ in effecting the resolution of synthetical asymmetric substances containing hydroxy- or amino-groups. Of the optically active amines, which are most readily obtainable, bornylamine and menthylamine appear to be best adapted for this purpose.

As the result of a series of brilliant investigations, Forster (Trans., 1898, 63, 390, &c.) has characterised pure bornylamine, so that its preparation can be readily carried out and the purity of the product ascertained.

The literature relating to the menthylamines affords evidence that the liquid described as *l*-menthylamine is in reality a mixture. Since a new asymmetric carbon atom is formed when menthoneoxime is reduced, theory indicates the production of more than one lævorotatory menthylamine. During the course of our investigations, a paper has been published by Tutin and Kipping (this vol., p. 65), in which this question is fully discussed and methods are described for the separation of some salts of four isomeric lævorotatory menthylamines. We had also obtained evidence of the existence of several lævorotatory menthylcarbimides, and the results relating to this portion of the work will be published shortly.

It has also been found that the reactions between pure *l*-menthylcarbimide and the alcohols proceed with velocities which are easily measured by means of the change in the rotations of the solutions.

The velocity of the reaction is influenced considerably by temperature, by various catalytic agents, by the solvent, and by the constitution of the alcohol. This variation affords a method of contrasting the reactivity of the alcohols in a homologous series.

*Preparation of Bornylcarbimide and 1-Menthylcarbimide.*

The carbimides,  $RN:CO$ , have been prepared by Hofmann's well-known method of distilling the corresponding ethyl carbamates,  $RNH \cdot CO_2Et$ , with phosphoric oxide, these operations being carried out under reduced pressure. At first it was feared that this method would cause racemisation. However, we have carried out over a hundred of these distillations, and have checked the specific rotations at all stages of the process of purification. The specific rotations of various preparations have been found to be uniform, and the specific rotations of the carbimides described are unaltered by repeated distillation over phosphoric oxide.

For the preparation of the following bornyl and neobornyl compounds, a mixture of bornylamine and neobornylamine hydrochlorides was first prepared by the reduction of camphoroxime by sodium in amyl-alcoholic solution; this was then fractionally crystallised until the two hydrochlorides were obtained with the specific rotations given by Forster (*loc. cit.*).

*Ethyl Bornylcarbamate,  $C_{10}H_{17} \cdot NH \cdot CO_2 \cdot C_2H_5$ .*

An aqueous solution of nineteen grams (1 mol.) of bornylamine hydrochloride is mixed with an excess of sodium hydroxide solution and extracted with light petroleum. The extract was mixed with an excess of sodium hydrogen carbonate and heated in a reflux apparatus with 10.8 grams (1 mol.) of ethyl chlorocarbonate. The mixture was then washed with water and the light petroleum extract separated and dried with calcium chloride. After distilling off the petroleum, the oily ester gradually forms a white solid, the yield being practically quantitative. The compound is volatile in steam, insoluble in water, but soluble in the ordinary organic solvents; it crystallises from light petroleum in hard, prismatic crystals or from aqueous ethyl alcohol in clusters of prismatic needles which melt at  $89^\circ$ .

0.2233 gave 12.2 c.c. moist nitrogen at  $16^\circ$  and 754 mm.  $N = 6.31$ .

$C_{13}H_{23}O_2N$  requires  $N = 6.22$  per cent.

0.5635, made up to 25 c.c. with chloroform, gave  $\alpha_D^* + 0.29^\circ$ , whence  $[\alpha]_D + 6.43^\circ$ .

\* In every case, unless otherwise specified,  $\alpha_D$  was determined in a 2 dm. tube.

0.5480, made up to 25 c.c. with benzene, gave  $\alpha_D + 0.21^\circ$ , whence  $[\alpha]_D + 4.79^\circ$ .

Some of the compound was distilled in steam, and its specific rotation taken as soon as its weight had become constant in a desiccator.

0.3775, made up to 25 c.c. with benzene, gave  $\alpha_D + 0.15^\circ$  as a mean of six concordant readings, whence  $[\alpha]_D + 4.96^\circ$ .

*Bornylcarbimide*,  $C_{10}H_{17}\cdot N:CO$ .

For the preparation of this compound, the pure ethyl bornylcarbamate is finely ground and distilled under reduced pressure in portions of three grams with twice its weight of phosphoric oxide. The slightly yellow distillate obtained after two fractionations boils at  $114-116^\circ$  under 14 mm. pressure, and on cooling solidifies to a soft, white, crystalline paste, the yield being about 70 per cent. The substance is very volatile, and has a characteristic odour, its solution in ether being particularly pungent. When dried on a porous plate, it melts at  $69^\circ$ . It is volatile in steam, and when warmed for some time with aqueous ammonia yields bornylcarbamide, melting at  $174^\circ$  (Forster gives  $175^\circ$ , *loc. cit.*).

0.1506 gave 10.6 c.c. moist nitrogen at  $21^\circ$  and 760 mm.  $N = 8.00$ .

$C_{11}H_{17}ON$  requires  $N = 7.82$  per cent.

0.2900, made up to 25 c.c. with benzene, gave  $\alpha_D + 1.14^\circ$  ( $c = 4.5$ ), whence  $[\alpha]_D + 49.14$ ; Forster and Attwell (*Proc.*, 1904, 20, 91) give  $[\alpha]_D + 46.5^\circ$ , where  $c = 2$ .

Several attempts to induce the polymerisation of the compound to the corresponding isocyanurate led to no definite result.

*Dibornylcarbamide*,  $OC:(NH\cdot C_{10}H_{17})_2$ .

When bornylcarbimide is heated with water in a rellux apparatus for several hours, carbon dioxide is evolved and the oil gradually solidifies; the latter is then collected and crystallised from aqueous alcohol. If the solution is allowed to evaporate slowly, the substance crystallises in lustrous needles often several centimetres in length; it is insoluble in water, benzene, or acetone, fairly so in ether, chloroform or in hot alcohol. It is volatile in steam, and does not melt below  $290^\circ$ , but can be sublimed at a slightly higher temperature, forming small, lustrous needles.

0.1707 gave 12.8 c.c. moist nitrogen at  $17^\circ$  and 742 mm.  $N = 8.49$ .

$C_{21}H_{36}ON_2$  requires  $N = 8.43$  per cent.

0.2724, made up to 25 c.c. with chloroform, gave  $\alpha_D + 0.35^\circ$  in a 1 dm. tube; whence  $[\alpha]_D + 32.12^\circ$ .

The neobornylamine hydrochloride was similarly treated in order to ascertain if the formation of the corresponding carbimide would facilitate the isolation of pure neo-derivatives, since there is a possibility that the neobornylamine obtained by Forster contains another isomeride, also produced in the reduction of camphoroxime.

*Ethyl Neobornylcarbamate*,  $C_{10}H_{17}\cdot NH\cdot CO_2\cdot C_2H_5$ .

The neobornylamine hydrochloride obtained in the manner indicated was treated in an exactly similar manner to the bornyl compound.

The carbamate thus produced is a white substance, which takes much longer to solidify than its isomeride; it is soluble in all organic solvents, but insoluble in water; it melts at  $36^\circ$ .

0.2419 gave 14.4 c.c. moist nitrogen at  $21^\circ$  and 758 mm.  $N = 6.75$ .

$C_{13}H_{23}O_2N$  requires  $N = 6.22$  per cent.

0.5189, made up to 25 c.c. with benzene, gave  $\alpha_D - 0.40^\circ$ ; whence  $[\alpha]_D - 9.63^\circ$ .

*Neobornylcarbimide* (?).

When the foregoing carbamate is distilled with phosphoric oxide, it yields an oil which is apparently a mixture, as it deposits a crystalline solid having  $[\alpha]_D - 13.4^\circ$ , whilst the mother liquor has  $[\alpha]_D - 1.1^\circ$ . These results seem to indicate a method of obtaining pure neobornyl derivatives, but this portion of the investigation has not been carried further.

*l-Menthylamine Derivatives*.\*

*l-Menthylcarbimide*,  $C_{10}H_{19}\cdot N\cdot CO$ .

Recrystallised menthoneoxime (from Kahlbaum's menthone,  $[\alpha]_D$  about  $-27^\circ$ ) is reduced in the usual manner with sodium and ethyl alcohol. The menthylamine (1 mol.) is dissolved in light petroleum in which an excess of sodium hydrogen carbonate is suspended, and heated in a reflux apparatus for  $1\frac{1}{2}$  hours with a solution of ethyl chlorocarbonate (1 mol.) in light petroleum, the product being worked up in the manner described under ethyl bornylcarbamate. The ethyl menthylcarbamate thus obtained melts at  $54-59^\circ$ , and various preparations dissolved in chloroform had  $[\alpha]_D$  ranging from  $-64.6^\circ$  to  $-68.9^\circ$ . The crude carbamate was distilled under reduced pressure in portions of three grams with  $1\frac{1}{2}$  times its weight of phosphoric oxide. The distillate is colourless and comes over from  $90-160^\circ$ , when the pressure varies from 20 to 40 mm. Various portions of the dis-

\* The term "*l*-menthylamine" is used for the pure *l*-menthylamine described by Tutin and Kipping (*loc. cit.*), and not for the mixture previously described in the literature under this name.

tillate vary in viscosity and in specific rotation. When fractionated under 10—13 mm. pressure, the greater portion distils at 108—110°. After three distillations, a product is obtained with a constant rotation and boiling point; this compound should be stored in sealed tubes.

The pure *l*-menthylcarbimide is a colourless, refractive, mobile liquid with a characteristic odour and the properties common to carbimides.

0.1822 gave 12.6 c.c. moist nitrogen at 16° and 742 mm.  $N = 7.87$ .

$C_{11}H_{19}ON$  requires  $N = 7.73$  per cent.

0.5544, made up to 25 c.c. with benzene, gave  $\alpha_D - 2.43^\circ$ ; whence  $[\alpha]_D - 54.79^\circ$ .

0.5548, made up to 25 c.c. with benzene, gave  $\alpha_D - 2.44^\circ$ ; whence  $[\alpha]_D - 54.97^\circ$ .

The ethyl-alcoholic solutions, when freshly prepared, gave the following values of  $[\alpha]_D$ :  $-53.83^\circ$  ( $t = 24.5^\circ$ ),  $-52.37^\circ$  ( $t = 33^\circ$ ),  $-51.71^\circ$  ( $t = 38^\circ$ ),  $-51.02^\circ$  ( $t = 50^\circ$ ).

Attempts to induce the polymerisation of the carbimide were not successful.

*Methyl l-Menthylcarbamate*,  $C_{10}H_{19} \cdot NH \cdot CO_2 \cdot CH_3$ .

This compound is easily obtained when the carbimide is heated in a reflux apparatus with an excess of methyl alcohol. After evaporating off the excess of alcohol, the residual oil soon solidifies, and is crystallised from light petroleum in long, lustrous needles. It melts at 53° and is soluble in the ordinary organic solvents.

0.1764 gave 10.6 c.c. moist nitrogen at 17° and 748 mm.  $N = 6.86$ .

$C_{12}H_{23}O_2N$  requires 6.57 per cent.

0.7840, made up to 25 c.c. with chloroform, gave  $\alpha_D - 2.33^\circ$  in a 1 dm. tube; whence  $[\alpha]_D^{16^\circ} - 74.29^\circ$ .

0.6996, made up to 25 c.c. with methyl alcohol, gave  $\alpha_D - 2.13^\circ$  in a 1 dm. tube; whence  $[\alpha]_D^{16^\circ} - 76.11^\circ$ .

*Ethyl l-Menthylcarbamate*,  $C_{10}H_{19} \cdot NH \cdot CO_2 \cdot C_2H_5$ .

The ethyl ester is prepared in exactly the same manner as the preceding compound. If molecular proportions of the carbimide and ethyl alcohol are left in a sealed tube for some weeks, hard, prismatic crystals gradually separate which, after crystallisation from aqueous alcohol, melt at 59°. This ester is volatile in steam and soluble in the ordinary organic solvents.

0.1043 gave 5.8 c.c. moist nitrogen at 18° and 752 mm.  $N = 6.35$ .

$C_{13}H_{25}O_2N$  requires  $N = 6.17$  per cent.

0.5131, made up to 25 c.c. with chloroform, gave  $\alpha_D - 2.85^\circ$ ; whence  $[\alpha]_D^{21} - 69.43^\circ$ .

0.5843, made up to 25 c.c. with ethyl alcohol, gave  $\alpha_D - 3.15^\circ$ ; whence  $[\alpha]_D - 67.39^\circ$ .

*Propyl l-Menthylcarbamate*,  $C_{10}H_{19} \cdot NH \cdot CO_2 \cdot C_3H_7$ .

This compound, which is obtained like the other esters, which it closely resembles, crystallises from petroleum in needles melting at  $57^\circ$ .

0.2013 gave 10.8 c.c. moist nitrogen at  $18^\circ$  and 750 mm.  $N = 6.11$ .  
 $C_{14}H_{27}O_2N$  requires  $N = 5.80$  per cent.

0.5889, made up to 25 c.c. with chloroform, gave  $\alpha_D - 3.23^\circ$ ; whence  $[\alpha]_D - 68.56^\circ$ .

0.5215, made up to 25 c.c. with propyl alcohol, gave  $\alpha_D - 2.82^\circ$ ; whence  $[\alpha]_D - 67.59^\circ$ .

*Di-l-menthylcarbamide*,  $OC \cdot (NH \cdot C_{10}H_{19})_2$ .

When *l*-menthylcarbimide is heated in a reflux apparatus with water, the oil gradually becomes pasty and then solid. The product can be crystallised from aqueous ethyl alcohol in long, stout needles which melt at  $258^\circ$ ; it is insoluble in water, fairly soluble in alcohol or ether, and readily so in chloroform or pyridine.

0.1392 gave 0.3805  $CO_2$  and 0.1482  $H_2O$ .  $C = 74.6$ ;  $H = 11.8$ .  
 $C_{21}H_{40}ON_2$  requires  $C = 75.0$ ;  $H = 11.9$  per cent.

0.4128, made up to 25 c.c. with ethyl alcohol, gave  $\alpha_D - 3.03^\circ$ ; whence  $[\alpha]_D - 91.75^\circ$ .

0.4595, made up to 25 c.c. with moist pyridine, gave  $\alpha_D - 3.41^\circ$ ; whence  $[\alpha]_D - 92.76^\circ$ .

TECHNICAL SCHOOL,  
 BLACKBURN.

LXXI.—*Hydrocellulose.*

By CHARLES FREDERICK CROSS and EDWARD JOHN BEVAN.

THE recent contribution of A. L. Stern (this vol., pp. 336—340) bearing the title "The so-called hydrocellulose" is based on experimental matter of obvious value, which may be taken as being beyond criticism, but the author's interpretations appear to us to be somewhat at variance with accepted facts and liable to misconstruction.

This appears in the title itself, which must be read in the light of the context supplied by one of the concluding paragraphs, where the author says :

"It is evident . . . that when cellulose is exposed to the action of hot dilute acids there is no formation of hydrocellulose . . . . The cellulose residue . . . . does not differ in elementary composition from the original, but has been converted into a fine powder . . . . A microscopic examination . . . . shows that the disintegration is due to the fact that certain portions of the fibres are more easily attacked than others, and when these portions are converted into soluble products the whole fibre falls to pieces."

We do not propose to discuss these statements in detail, but with all possible brevity to emphasise some antecedent facts, which, although of critical importance in this connection, have apparently been overlooked.

(1) The author's criticisms of the work of A. Girard are scarcely justified, because the three methods for the production of the typical hydrocelluloses carefully described by the French chemist (*Memoire sur l'Hydrocellulose et ses derivees*, Paris, 1881) are in no case followed.

(2) The question as between an empirical formula  $C_{12}H_{20}O_{10}$  or  $C_{12}H_{22}O_{11}$  for the products described by Girard as the typical hydrocelluloses is therefore not raised by the fact that the author has obtained, under other conditions, residues which have the empirical composition  $C_{12}H_{20}O_{10}$  of the original cellulose.

(3) On the other hand, we submit that these residues are constitutionally different from the original celluloses. They are attacked by dilute alkaline solutions, are largely soluble in 15—20 per cent. caustic soda solutions, are oxidised by Fehling's solution, and generally show differences in the reactivity of the typical carbonyl and hydroxyl groups. Their behaviour towards nitric acid, acetic anhydride, and esterifying reagents generally differs from that of the original cellulose, and the properties of the corresponding derivatives are also different.

Girard studied this part of the subject in detail, in regard to the typical hydrocelluloses, and his results have been frequently confirmed.

(4) The main point which Stern appears to overlook is that structure in the celluloses is bound up with chemical composition and constitution. The structural properties of cellulose and hydrocellulose persist in their esters, and also through a cycle of reactions such as is involved in the conversion into xanthate and the regeneration of the cellulose (or hydrocellulose) from this condition of combination.

This very important point has closely engaged the attention of investigators, and considerable positive evidence has already been accumulated showing that the structural properties of cellulose are a function of the actual molecular aggregate taken in the chemical sense.

Incidentally we would emphasise this point, that it is at present easily open to chemists to settle any question as to chemical changes in cellulose, independently of structure, by operating on the homogeneous, structureless forms of this compound now available.

Without extending our criticism to lesser details, we conclude that the sub-group connoted by the term "hydrocellulose" remains unaffected by Stern's investigations save as regards his useful contribution of new matter.

Finally, in order to illustrate the actual state of our knowledge of the sub-group in question, we may point out:

That the normal cellulose (anhydride) is chemically labile, as it is a structurally plastic aggregate, occupying a middle position between the two extremes, determined by treatment (*a*) with alkali hydroxides, (*b*) with halogen hydracids, both in presence of water.

These extremes are both chemical and structural; under (*a*), the carbonyl groups show no reactivity and may be assumed to occupy a ketonic or cyclo-ketonic position in the aggregate: under (*b*), they become distinctly aldehydic, and in fact the aggregate is partly resolved with the production of free aldoses.

Structurally, the maximum of integration is attained under (*a*), whilst the maximum of disintegration is reached under (*b*).

This very wide range of variation falls mainly within the limits of hydroxyl reactions; the direct effects produced are those of hydration and hydrolysis, with the complementary phenomena of reversion.

In the case of the alkali hydroxides, the reactions, including the phenomena of "mercerisation" are chiefly those of hydration, some hydrolysis probably accompanying the effects, but without resolution of the cellulose to soluble forms, at least in the case of the normal cotton cellulose.

With acids, it appears that the hydrolysis which occurs and which, in fact, proceeds to the extreme limits—since the cellulose is partly resolved into the simple aldose—is accompanied by effects of reversion. The substances described by Stern have the character of reverted products.

In either case, it is obvious that the empirical composition of a final

residue throws but little light on the changes it may have undergone. In many such reactions, the alterations in composition are fractional, but it is none the less evident that profound constitutional changes occur.

A terminology for the brief expression of these classified effects must for the present remain on a conventional basis.

It would be convenient to retain the terms which have hitherto been current, namely, hydracellulose and hydrocellulose. The former might be limited to the products of the action of alkalis on cellulose, which are certainly hydrates; hydrocellulose, on the other hand, might be applied to the products of acid reactions, which are certainly hydrolysed, although in many cases showing the empirical composition of the original anhydride.

The latter have many properties in common with the "hemicelluloses," a term which is useful in designating a group of natural, mostly cellular, celluloses, which are distinct from the fibrous celluloses in chemical constitution as well as in structure and function in plant life ("*Cellulose*," Cross and Bevan, p. 87). This term might be very well extended to include the hydrocelluloses, if the suppression of the latter designation be considered advisable.

Whatever terminology may be finally adopted, it is important that in the meantime the empirical facts should be kept clearly expressed, and our purpose in this contribution is to prevent the confusion of issues which is likely to result from the theoretical views set forth in the paper now under discussion.

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## LXXII.—*The Slow Combustion of Ethane.*

By WILLIAM ARTHUR BONE and WILLIAM ERNEST STOCKINGS.

THE present paper contains some further results of the investigation of the slow combustion of hydrocarbons, at temperatures below their ignition points, initiated by one of us in conjunction with Mr. Wheeler (Trans., 1902, 81, 536; 1903, 83, 1074). The experimental part comprises three sections dealing respectively with: (1) the interaction of ethane and oxygen at 250–400°, under pressures of 1.75 to 2.33 atmospheres, in borosilicate glass bulbs; (2) the oxidation of ethane at 400–500°, under reduced pressure, in our "circulation apparatus"; and (3) the slow combustion of ethyl alcohol and acetaldehyde.

As will be readily understood, the case of ethane has proved more complex than that of methane; this is partly due to the greater

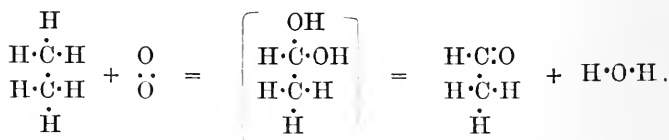
number of stages involved in the combustion of ethane, and partly also to the disturbing influences of secondary processes which were entirely absent in the methane experiments. The precise significance of the various phenomena under discussion, in relation to the general question of the combustion of hydrocarbons, can perhaps only be correctly gauged after a careful perusal of the evidence contained in our account of the actual experiments, but it may assist the reader if we now summarise our main conclusions.

(1) Under similar conditions, ethane burns much more rapidly than methane, and in borosilicate glass bulbs both hydrocarbons are oxidised at temperatures much below the limiting temperature (about  $400^{\circ}$ ) at which, under similar conditions, steam is appreciably formed from electrolytic gas.

(2) When ethane reacts with a quantity of oxygen insufficient to burn the whole of it to carbon monoxide and steam, there is no preferential combustion either of hydrogen or of carbon. In the absence of the disturbing effects of secondary processes, the interaction is always marked by a diminution in the pressure of the cold products, without any deposition of carbon or liberation of hydrogen.

(3) On the other hand, the combustion proceeds in several well-defined stages, during which the oxygen enters into, and is incorporated with the hydrocarbon molecule forming oxygenated intermediate products.

(4) The first stage we have been able to distinguish in the process involves the rapid formation of acetaldehyde and steam. It may perhaps be best represented as a process of hydroxylation, followed by the immediate decomposition of the unstable hydroxylated product, thus:



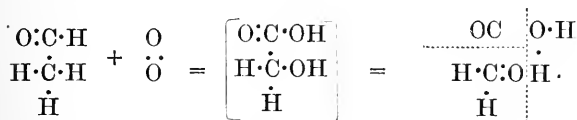
There is no direct evidence of the primary formation of any ethyl alcohol in our experiments such as would be required by the general theory of combustion recently advanced by Professor Armstrong (*Trans.*, 1903, 83, 1088). But as we find that ethyl alcohol is, under similar conditions, oxidised far more rapidly than ethane itself, we cannot attach any significance to its non-occurrence among the oxidation products of ethane.\* In this connection we would remark

\* Since the above was written, however, one of us, in conjunction with Dr. Julien Drugman, has detected ethyl alcohol among the products of the interaction of ethane and ozone at  $100^{\circ}$  (*Proc.*, 1904, 20, 127). It is therefore highly probable that ethyl alcohol is really the primary oxidation product.

that, whilst the proportions of ethane and oxygen most favourable to chemical change appear to be 1 : 1, that is, equimolecular, interaction takes place nearly as rapidly in mixtures of 2 volumes of ethane to 1 volume of oxygen.

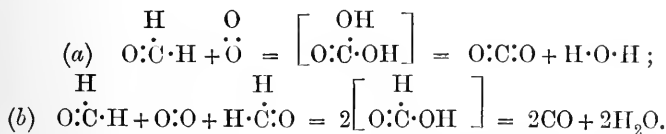
(5) The second stage, which is also a very rapid one, involves the breaking down of the original hydrocarbon structure,  $\cdot\dot{\text{C}}\cdot\dot{\text{C}}\cdot$ , and the formation of formaldehyde, carbon monoxide, and steam.

This stage may also conceivably be regarded as a process of hydroxylation, if we assume the intermediate formation of glycollic acid which immediately decomposes, thus :



That this is a very prominent stage in the sequence of the oxidation phenomena is proved by our circulation experiments. In one of these experiments (No. 5, page 720) as much as 80 per cent., and in another (No. 2, page 717) over 90 per cent., of the ethane burnt appeared in the final products as formaldehyde, carbon monoxide (or its oxidation product, carbon dioxide), and steam.

(6) The formaldehyde finally undergoes further oxidation to carbon monoxide, carbon dioxide, and steam, probably as the result of two simultaneous reactions, namely :

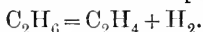


There was certainly some evidence of the intermediate formation of formic acid in our experiments.

This third stage appears to be somewhat slower than the two preceding stages, a circumstance which, under suitable conditions, leads to a considerable accumulation of aldehyde vapours during an experiment.

(7) Hydrogen, or methane, or both, may appear in the products, without any carbon being liberated, as the result of the purely thermal decomposition of formaldehyde and acetaldehyde vapours respectively, more particularly when there is a large accumulation of these during an experiment. Under the conditions of our bulb experiments, we have proved that acetaldehyde does decompose in accordance with the equation  $\text{CH}_3\cdot\text{CHO} = \text{CH}_4 + \text{CO}$ . Formaldehyde also yields hydrogen and carbon monoxide, although its decomposition is a more complex process than that of acetaldehyde.

(8) A little ethylene and hydrogen may appear in the products as the result of the purely thermal decomposition of ethane itself:



(9) Carbon is not liberated below the ignition points of the reacting mixtures. If, however, the experimental conditions are such that the heat liberated during the initial stages of oxidation is sufficient to raise the temperature of the reacting gases to the ignition point, an explosion occurs, during which the excess of hydrocarbon, and probably also aldehyde vapours, are decomposed with liberation of carbon and hydrogen, together with some acetylene and ethylene.

(10) The view taken of the mechanism of the combustion of ethane is supported by the experiments on the combustion of ethyl alcohol and acetaldehyde.

## EXPERIMENTAL.

### PART I.

*The Interaction of Ethane and Oxygen in Borosilicate Glass Bulbs at Temperatures between 250° and 400°.*

#### *Preparation and Composition of Original Mixtures.*

The ethane was prepared by the action of water on zinc ethide mixed with sand; the average yield was about 3 litres of gas from every 10 grams of ethide decomposed, and the purity of the gas is shown by the following explosion analysis:

					mm.
Gas taken...	...	...	...	27.8	} Total 545.2.
Oxygen and air added	...	...	...	517.4	
Ratio...	Diluents			= 3.4.*	
	Explosive mixture				
Contraction (C)	...	...	...	69.0	} C/A = 1.250.
Absorption (A)	...	...	...	55.2	
Therefore ethane = 27.6 = 99.3 per cent.					

The oxygen was obtained by heating recrystallised potassium permanganate. The mixtures of ethane and oxygen were made and stored in graduated glass holders over glycerin diluted with its own volume of water; both gases are practically insoluble in this liquid, and the composition of a particular gaseous mixture was not appreciably

\* We find it necessary in analysing ethane, or mixtures of ethane and oxygen, to dilute the explosive mixture,  $2\text{C}_2\text{H}_6 + 7\text{O}_2$ , with at least three times its own volume of excess of air or oxygen. Otherwise some of the hydrocarbon is decomposed by the shock of the explosion, carbon is deposited, and the ratio C/A may work out to 1.30, or even higher, instead of the theoretical 1.250.

altered even after prolonged contact with it. Usually, however, the mixtures were used for the experiments within 48 hours of their preparation. Most of our experiments were made with mixtures of equal volumes of the two gases, these proportions being, as we found, very favourable to rapid chemical change.

We also employed mixtures of ethane and oxygen in the ratios 2 : 1, 1 : 2, 1 : 3·5, and 1 : 3·75, and in one or two experiments we used mixtures of ethane and air. The amounts of adventitious nitrogen in our mixtures of ethane and oxygen were always very small, usually less than 0·5, and never more than 1·5 per cent. Following the rule adopted in previous papers, we propose to leave this nitrogen out of the reckoning altogether, and to express the compositions of the various gaseous mixtures, as well as pressure records, in terms of the nitrogen-free gas.\* The following table gives the exact composition of the various nitrogen-free mixtures employed, as well as the ratio C/A obtained in the analysis of each by the explosion method. We should perhaps add that the oxygen was in each case determined by absorption with a freshly prepared and strongly alkaline solution of pyrogallol, in which we found ethane to be insoluble.

TABLE I.

Mixture.	A.	B.&C.	D.	E.	F.	G.	H.	K.	L.
Ethane .....	50·6	49·8	49·5	49·7	50·3	66·65	32·2	22·8	21·05
Oxygen .....	49·4	50·2	50·5	50·3	49·7	33·35	67·8	77·8	79·95
C/A .....	1·246	1·247 1·250	1·253	1·247 1·251	1·255	1·248	1·260		

*Analysis of the Gaseous Products of Reaction.*

The products of reaction usually contained carbon dioxide, carbon monoxide, unchanged ethane, and oxygen. Occasionally also small quantities of aldehyde vapours were present, as well as some methane and free hydrogen. We found that aldehyde vapours could be removed, without appreciably affecting the relative proportions of the other products, simply by exposing the gases to a thin layer of strong sulphuric acid for about five minutes.

The carbon dioxide, carbon monoxide, and oxygen were then re-

\* Since, in analysing the various mixtures, nitrogen was always estimated "by difference," after all other constituents had been determined, the percentage composition of our nitrogen-free gases will always add up to 100.

moved and estimated in the following order, namely: (1) carbon dioxide, by means of strong caustic potash solution; (2) oxygen, by means of freshly prepared and strongly alkaline pyrogallol solution; (3) carbon monoxide, by agitating for 5 minutes with a freshly prepared ammoniacal solution of cuprous chloride previously saturated with ethane; before the final remeasurement, the gas was exposed to a layer of dilute sulphuric acid.\* The residual gas was afterwards exploded with a large excess of oxygen and air, and the ratio C/A determined. A ratio higher than 1.255 was always taken as an indication of the presence of either methane or free hydrogen in the products. In such a case, a second explosion analysis of the residual gas was usually made after it had been exposed to the action of "oxidised" palladium sponge at 100°, in order to determine the relative proportions of methane and hydrogen present.

*The Bulb Experiments at 200° to 400°.*

The mixtures of ethane and oxygen were sealed up, at atmospheric temperatures and pressures, in cylindrical borosilicate glass bulbs which were afterwards kept at constant temperatures between 200° and 400°. At the commencement of the reaction the hot gases would, therefore, be under pressures varying between 1.75 and 2.33 atmospheres, according to the temperature of the bath. The only departure from the experimental procedure described in a previous paper (Trans., 1902, 81, 535) was the adoption of a more accurate method of estimating the contraction observed when the cooled bulbs were opened under mercury. After the gaseous products had been removed for analysis through a Töpler pump, the bulbs were rinsed out with 2 or 3 c.c. of distilled water, and the rinsings tested for aldehydes and acids with Schiff's reagent and litmus respectively.

In tabulating the results of the various experiments, we shall in each case give (1) the index letter of the mixture employed; (2) the temperature and pressure at which the bulbs were filled; (3) the duration of heating; (4) the corrected change in volume (in most cases a contraction) expressed as percentage of the original volume; (5) the

\* We adopted this method for estimating carbon monoxide after a series of trial experiments on the analysis of mixtures of the monoxide and ethane in known proportions. The solubility of ethane in an ammoniacal solution of cuprous chloride, although very small, is quite appreciable.

No acetylene was ever detected in the products, except in one or two of the bulb experiments where the original mixtures of ethane and oxygen exploded. On the other hand, the products occasionally contained a small amount of ethylene, which would, of course, be removed along with the carbon monoxide by the ammoniacal cuprous chloride solution. The separate estimation of the two gases was always made in a special independent analysis.

composition of the nitrogen-free gaseous products; (6) the ratio C/A found in the explosion analysis of the residual gas after removal of carbon monoxide, carbon dioxide, and oxygen; (7) the ratio  $\text{CO}/\text{CO}_2$  in the gaseous products.

*Experiments at 200° and 225°.*

Four out of six bulbs filled with mixture D ( $\text{C}_2\text{H}_6 = 49.5$ ;  $\text{O}_2 = 50.5$ ) were kept at 200–205° for 9 days; there was no appreciable change in any one of them. The other two bulbs were then kept at 225° for a week; the formation of water was observed in one of them after four days, and in the other at the end of the experiment. The nitrogen-free gaseous products from the first bulb contained  $\text{CO}_2 = 1.5$ ,  $\text{CO} = 2.8$ ,  $\text{C}_2\text{H}_6 = 47.7$ , and  $\text{O}_2 = 48$  per cent., but no hydrogen.\*

*Experiments at 250°.*

At this temperature, no change was observed in the case of three bulbs containing a mixture of 2 volumes of ethane with 1 volume of oxygen after 48 hours. When, however, the gases were mixed in equimolecular proportions, they reacted with fair velocity, which varied considerably with the 'surface factor' of each bulb. In one out of five bulbs (No. 1, Table III) it will be seen that the whole of the oxygen disappeared within 17 hours, and in another (No. 5) after 48 hours. The reaction was characterised by the continuous formation of steam, and also of aldehydes, as was evident when we applied Schiff's test to the rinsings from the bulbs at the conclusion of each experiment. In no case was there any deposition of carbon, or liberation of hydrogen, but in all cases the cooled products showed a large contraction in volume when the bulbs were open under mercury. In bulbs Nos. 1 and 5, about 56 per cent. of the original ethane remained intact at the end of the reaction.

\* The lowest temperature at which any change could be detected in mixtures of methane and oxygen, similarly heated in borosilicate glass bulbs, was 300°, and even then the heating had to be continued for two or three weeks (Trans., 1902, 81, 546). Further, the limiting temperature at which steam is appreciably formed from electrolytic gas under similar conditions is about 400°.

TABLE II.

Bulbs 1 and 2 were originally filled with mixture B at 10° and 765 mm.  
 „ 3, 4, and 5 „ „ „ C „ 13° and 755 „

Bulb No.* .....	1	2	3	4	5
Duration of heating in hours .....	17	25	48	48	48
Percentage contraction (corr.)* .....	34.8	25.7	20.3	30.3	36.5
Percentage composition of the nitrogen-free gaseous products.					
{ Carbon dioxide...	15.9	10.35	9.25	13.4	18.2
{ Carbon monoxide	41.2	23.15	18.25	29.3	37.8
{ Oxygen .....	nil	19.10	25.30	10.7	nil
{ Ethane .....	42.9	47.40	47.20	46.6	44.0
C/A for 'residual gas' .....	1.250	1.250	1.250	1.248	1.245
CO/CO <sub>2</sub> .....	2.60	2.23	1.97	2.19	2.08

\* The formation of condensable intermediate products is proved by the magnitude of the contractions observed in bulbs 1 and 5. For combustion to CO, CO<sub>2</sub>, and H<sub>2</sub>O only, these contractions would have been 31.7 and 31.9 per cent. respectively.

There was no acetylene in the gaseous products, but, in the case of one or two of the bulbs, possibly a small amount of ethylene (under 1 per cent.) was present; this would be included in the figures for CO.

Since it has been shown that no change occurs when the following pairs of gases are kept at 250°, or even at much higher temperatures, in borosilicate glass bulbs for very long periods of time (Trans., 1902, 81, 538—593), namely, (a) hydrogen and oxygen (electrolytic gas), (b) methane and oxygen, (c) moist carbon monoxide and oxygen, it may be concluded from the foregoing experiments:

(I) That in the primary oxidation of ethane there is no selective combustion either of carbon or of hydrogen.

(II) That no methane is liberated during the breaking down of the ethane molecule as the result of oxidation pure and simple. This, in view of some later results, is an important point.

(III) That the large quantity of carbon dioxide in the gaseous products did not arise from the secondary oxidation of carbon monoxide.

*Experiments at 300°.*

A large number of experiments were made at this temperature with mixtures in which the proportions of ethane and oxygen were varied between 2:1 and 1:3.75, and the results are extremely interesting from the point of view adopted in this paper as to the course of the oxidation. A significant feature was the surprisingly rapid oxidation always observed with the mixtures containing ethane and oxygen in the ratio 2:1 or 1:1, as compared with the much slower ratio exhibited by other mixtures containing higher proportions of oxygen.

*(1) With Mixtures of 2 Volumes of Ethane and 1 Volume of Oxygen.*

(a) Two bulbs, filled with mixture G at 18° and 760 mm., were maintained at 300° for 30 minutes. On cooling, water condensed on the inner surfaces, and soon afterwards minute oily particles appeared, due, as we afterwards found, to a rapid polymerisation of aldehyde vapours. No carbon separated. The contractions observed when the bulbs were opened under mercury were 23.6 and 29.3 per cent. respectively. The products contained hydrogen, and probably also some methane. The analytical results are shown in Table III (bulbs Nos. 6 and 7).

(b) In a second experiment, two bulbs, originally filled at 15° and 746 mm. with mixture G, were kept at 300° for 45 minutes. The appearance of the cooled bulbs was much the same as in the previous experiment, except that no separation of oily particles was observed. On opening the bulbs under mercury, we were surprised to find no contraction in volume; if anything, the gaseous products were under slight pressure. There was, however, an overpowering odour of aldehyde vapours, some of these polymerised in the connections of the Töpler pump when the gases were withdrawn from the bulbs for analysis. The rinsings from the bulbs gave a strong aldehydic reaction, but we were unable to detect any ethyl alcohol in them.

Analyses of the gaseous products, after the removal of aldehyde vapours, showed the entire absence of oxygen, and a very high ratio  $\text{CO}/\text{CO}_2$ . The ratios C/A obtained for the 'residual gas' in each case (1.616 and 1.650 resp.) indicated the presence of hydrogen, or methane, or both. On again analysing the gas after removal of hydrogen by means of oxidised palladium sponge at 100°, the ratio C/A fell to 1.343. Details of this experiment (bulbs 8 and 9) are given in Table III.

TABLE III.

Bulb No. ....		6	7	8	9
Duration of heating.....		30 mins.	30 mins.	45 mins.	45 mins.
Percentage contraction (corr.) .....		23·6	29·3	nil	
Percentage composition of the nitrogen-free gaseous products.	Carbon dioxide .....	3·6	6·8	1·90	2·50
	Carbon monoxide .....	15·7	28·2	36·20	35·15
	Oxygen .....	10·7	19·15	nil	0·20
	Ethane .....	—	—	36·50	35·45
	Methane .....	—	—	10·20	10·10
	Hydrogen .....	—	—	15·20	16·60
C/A for 'residual gas'.....		1·341	1·298	1·616	1·650
CO/CO <sub>2</sub> .....		4·36	4·15	19·0	14·0

The salient features of these experiments are (1) the very large formation of aldehydes (which in the case of bulbs 6 and 7 polymerised when the hot products were cooled), and (2) in the case of bulbs 8 and 9, the marked production of methane and hydrogen, accompanied as it was by an extraordinarily high ratio CO/CO<sub>2</sub>. This formation of methane and hydrogen cannot, as the experiments at 250° prove, be regarded as the result of the primary oxidation of the ethane; it is undoubtedly a secondary effect, connected, it would seem, with an excessive accumulation of aldehyde vapours during the experiment. It may, we think, be entirely ascribed to the purely thermal decomposition of acetaldehyde and formaldehyde vapours. We have proved that under the conditions of our bulb experiments at 300—400° acetaldehyde does undergo simple decomposition, at a moderate velocity, in accordance with the equation  $\text{CH}_3\cdot\text{CHO} = \text{CH}_4 + \text{CO}$ . The vapour of formaldehyde also, under similar conditions, decomposes, yielding carbon monoxide and hydrogen, but the process is not so simple as the case of acetaldehyde. As one of us is carrying out further experiments on the stabilities of these aldehydes at higher temperatures, we shall reserve details for a future communication.

(2) *With Mixtures of Equal Volumes of Ethane and Oxygen.*

In these experiments, the whole of the oxygen always disappeared within 30 to 45 minutes, and frequently even within 15 or 20 minutes, the

reaction being marked by the formation of aldehydes, steam, and carbon monoxide, together with smaller preparations of carbon dioxide. The ratio  $\text{CO}/\text{CO}_2$ , which for similar mixtures at  $250^\circ$  was 1.97 to 2.6 (see Table II), now rose to between 4 and 5. No carbon separated, neither was there any liberation of either hydrogen or methane; the rinsings from the bulbs always had a strong aldehydic reaction. More prolonged heating (see bulbs 12 and 13, Table IV) had little or no effect on the composition of the gaseous products; the ratio  $\text{C}/\text{A} = 1.260$  for the residual gas in the case of bulb 13 suggests the presence of a very small quantity of either hydrogen or methane.

TABLE IV.

Bulb No. * .....	10	11	12	13
Duration of heating.....	45 mins.	60 mins.	10½ hours.	23 hours.
Percentage contraction (corr.).....	37.6	38.6	36.8	34.4
Percentage composition of the nitrogen-free gaseous products. {				
Carbon dioxide ..	10.2	10.65	9.80	9.5
Carbon monoxide ..	47.7	45.30	48.25	45.0
Oxygen .....	nil	0.45	0.20	0.5
Ethane .....	42.1	43.60	41.75	45.0
C/A for 'residual gas' .....	1.250	1.247	1.254 1.249	1.260
Ratio $\text{CO}/\text{CO}_2$ .....	4.1	4.1	4.9	4.73

\* The gases contained neither ethylene nor acetylene.

The percentage contraction for these bulbs would have been only about 31 had the hydrocarbon been burnt to  $\text{CO}$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$  without the formation of intermediate condensable substances.

### (3) With Mixtures of 1 Volume of Ethane and 2 Volumes of Oxygen.

The rate of oxidation observed with these mixtures was on the whole distinctly less than in the experiments just recorded. In one experiment with five bulbs, two (Nos. 14 and 15, Table V) were removed from the air-oven after 90 minutes, the others were allowed to remain for  $16\frac{1}{2}$  hours longer.

Free oxygen still remained in the first two bulbs, but had practically all disappeared from the other three. In no case was carbon deposited or hydrogen liberated; there was an abundant formation of water,

carbon monoxide, and carbon dioxide. The rinsings from all the bulbs showed distinct aldehydic reactions.

The ratio C/A for the 'residual gas' after removal of carbon dioxide, oxygen, and carbon monoxide, was always found to be somewhat higher than 1.25, and was highest in the case of the bulb which had been heated longest. A second analysis of the 'residual gas,' after it had been exposed to the action of oxidised palladium sponge at 100°, gave ratio C/A not materially different from the corresponding values before treatment with palladium. We therefore concluded that the products contained small quantities of methane rather than hydrogen, and have interpreted the results accordingly. Probably this methane arose as the result of a purely thermal decomposition of acetaldehyde vapour.

The details for three of the above bulbs are given in Table V.

TABLE V.

Bulbs originally filled with mixture H at 12.5° and 733 mm.

Bulb No.....	14	15	16
Duration of heating .....	90 mins.	90 mins.	18 hours.
Percentage contraction (corr.) .....	39.5	35.7	44.5
Percentage composition of nitrogen-free gaseous products.			
{ Carbon dioxide .....	18.5	14.75	28.45
{ Carbon monoxide .....	50.9	34.60	59.10
{ Oxygen .....	15.9	25.40	0.20
{ Ethane .....	13.9	23.05	10.40
{ Methane.....	0.8	2.20	1.85
C/A for 'residual gas' .....	1.270	1.282	1.310
CO/CO <sub>2</sub> .....	2.75	2.35	2.10
The condensed water contained aldehydes.			

(3) *With Mixtures of 1 Volume of Ethane and 3½ Volumes of Oxygen.*

Although the mixture contained an amount of oxygen just sufficient to burn the hydrocarbon completely to steam and carbon dioxide, it is remarkable how very slowly, comparatively, the oxidation proceeded. We never, for example, detected any formation of

water within an hour, and even after two days a considerable quantity of oxygen, as well as some ethane, remained in the bulbs.

The results for two bulbs, originally filled with mixture K at 13° and 751 mm., are tabulated below.

TABLE VI.

No. of bulb .....	17	18
Duration of heating .....	17 hours.	48 hours.
Percentage contraction (corr.) .....	33·30	37·0
Percentage composition of the nitrogen-free gaseous products. {		
Carbon dioxide .....	15·05	20·80
Carbon monoxide .....	32·50	36·20
Oxygen .....	41·40	37·50
Ethane .....	8·05	5·50
CO/CO <sub>2</sub> .....	2·16	1·74

The rinsings from these bulbs showed a faint aldehydic reaction with Schiff's reagent, and also it may be shown by calculation that the original ethane and oxygen are not wholly accounted for in the gaseous products.

(4) *With a Mixture of 1 Volume of Ethane with 3·75 Volumes of Oxygen.*

Two bulbs, filled at 13·3° and 760 mm. with mixture L (ethane = 21·05; oxygen = 78·95), were kept in the air-bath at 300° for eight consecutive days. The oxidation was very slow, but eventually all the ethane disappeared. Nearly a third of the original oxygen still remained at the end of the experiment, the ratio CO/CO<sub>2</sub> in the gaseous products being 1·28 and 1·31 respectively. The rinsings from the bulb gave a very faint aldehydic reaction. Details of the experiment are given below.

TABLE VII.

Bulb No. ....	19	20
Duration of heating .....	8 days.	8 days.
Percentage contraction (corr.) .....	38.1	38.9
Percentage composition of gaseous products.		
{ Carbon dioxide .....	25.1	26.25
{ Carbon monoxide .....	33.9	33.55
{ Oxygen .....	41.0	40.20
CO/CO <sub>2</sub> .....	1.31	1.28

*Experiments at 350° to 400°.*

These experiments are chiefly interesting in that they throw some light on the cause of the separation of carbon during the incomplete combustion of hydrocarbons.

(1) A series of six bulbs, filled under atmospheric pressure with mixture B ( $C_2H_6 = 49.8$ ;  $O_2 = 50.2$ ), were kept in the air-bath at 350° for 40 hours. On withdrawing them, we were somewhat surprised to find their inner surfaces covered with a thick deposit of finely-divided carbon. Some water condensed on cooling, and on opening the bulbs under mercury, we found their contents to be under considerable pressure (1000—1100 mm.). The gaseous products contained much carbon monoxide and hydrogen, as well as smaller quantities of unsaturated hydrocarbons (including some 0.1 to 0.2 per cent. of acetylene), methane, ethane, and carbon dioxide. The composition of the gaseous products from two of the bulbs is given below.

TABLE VIII.

Bulb No. ....	21. ....	22.
Carbon dioxide .....	4.80 .....	4.35
Carbon monoxide.....	33.55 .....	33.60
Unsaturated hydrocarbons	2.50 .....	1.90
Hydrogen.....	48.80 .....	50.80
Methane .....	8.75 .....	7.90
Ethane.....	1.60 .....	1.45

Evidently, therefore, either the primary oxidation of the ethane had taken a different course at 350° from that indicated by experiments

at lower temperatures, or new secondary factors were being brought into play.

(2) The true explanation became clear when the apparatus was so arranged that we could watch the bulbs during the whole time of heating. Bulbs containing mixture F ( $C_2H_6=50.3$ ;  $O_2=49.7$ ) were employed. A bulb was introduced into the bath at  $400^\circ$ ; the temperature in the vicinity of the bulb immediately sank to  $350^\circ$ , then began to rise rather quickly to about  $375^\circ$ , afterwards more slowly. Nothing in particular was observed for a time, but after about four or five minutes, a bright flash was seen, accompanied by a sharp click and the appearance of a thick cloud of solid carbon particles. The bulb was at once removed. On allowing it to cool, some water condensed, and on nipping off the sealed end of the capillary tube inside a rubber joint connected with a capillary manometer, we found the gases to be under 1290 mm. pressure. The gaseous products, which had much the same composition as those obtained in the previous experiment, are indicated in the following table.

TABLE IX.

*Bulb No. 23. Mixture F.*

	Per cent.		Per cent.
Carbon dioxide.....	3.8	Methane .....	5.0
Carbon monoxide .....	34.3	Ethane .....	0.9
Hydrogen .....	54.1	Oxygen .....	0.4
Unsaturated hydrocarbons	1.5		—
			100.0

The experiment was repeated several times with similar results, which suggested the following view. At temperatures between  $350^\circ$  and  $400^\circ$ , the velocity of the primary oxidation (or of the initial stages of oxidation) is so great that the mixture of ethane, aldehyde vapours, and oxygen, is locally heated to above its ignition point (which is probably higher than  $400^\circ$ ). The result is an explosion, during which ethane, and possibly also aldehydes, are thermally decomposed with liberation of carbon and hydrogen. If, therefore, the velocity of the initial stage, or stages, could be damped, either by admixture of inert gas, or by using a very slow bulb, the oxidation might proceed normally to its end, in which case there should be no liberation of carbon or hydrogen. This was proved in the following experiments.

(3) Three bulbs, one (No. 24) known to be a very slow one, the other two (Nos. 25 and 26) being quick ones, filled under atmospheric pressure with mixture F, were placed side by side in the same air-bath at  $375^\circ$ . The temperature in the vicinity of the bulbs at once fell to

350°, then steadily rose during the next 15 minutes to 375°. The heating was continued for an hour longer. In the case of bulbs Nos. 25 and 26, the gases had ignited, and No. 26 was smashed by the force of the explosion. The inner surface of No. 25 was covered with finely-divided carbon, and water condensed on cooling. The contained gases were under 1100 mm. pressure. In the case, however, of bulb No. 24, there had been no explosion, and consequently no deposition of carbon; on cooling it, water condensed on its inner surface, and on opening under mercury there was a contraction of 38.4 per cent. of the original volume. There was no hydrogen in the gaseous products, but the rinsings from the bulb contained aldehydes. Table X shows the details of this very suggestive experiment.

TABLE X.

Bulbs filled with mixture F at 15° and 750 mm.

Bulb No. ....	24	25	26
Percentage change in volume .....	- 38.0*	+ 46	
Percentage composition of the nitrogen-free gaseous products. {			
Carbon dioxide .....	8.15	4.75	Bulb smashed by the force of the explosion.
Carbon monoxide .....	52.35	33.30	
Ethane .....	39.50	1.35	
Hydrogen.....	nil.	50.90	
Methane .....	nil.	7.90	
Unsaturated hydrocarbons.....	nil.	1.80	
C/A for 'residual gas' .....	1.250	8.9	
Ratio CO/CO <sub>2</sub> .....	6.42		

\* For combustion to CO, CO<sub>2</sub>, and H<sub>2</sub>O only, without the formation of condensable intermediate products, this would only have been - 30.8.

(4) We now damped the velocity of oxidation by dilution with nitrogen. Two bulbs, Nos. 27 and 28, were filled with mixture B (ethane = 49.8; oxygen = 50.2) diluted with about 8 per cent. of nitrogen. Two other bulbs, Nos. 29 and 30, were filled with a special mixture of ethane and air containing C<sub>2</sub>H<sub>6</sub> = 16.95; O<sub>2</sub> = 17.40; and N<sub>2</sub> = 65.65 per cent. Bulb 27 was kept at 390—400° for an hour, and No. 28 at the same temperature for 18 hours. Bulbs Nos. 29 and 30 were kept at 380—390° for 24 hours. The oxidation proceeded normally in all cases; all the oxygen disappeared, water and aldehydes were formed, but there was

neither separation of carbon nor liberation of hydrogen. The details of the experiments with bulbs Nos. 27 and 29 are given below.

TABLE XI.

Bulb No. ....	27	29
Duration of heating .....	1 hour	24 hours
Percentage contraction (corr.) .....	35	15
Percentage composition of the gaseous products. {		
Carbon dioxide .....	7.20	5.90
Carbon monoxide .....	44.20	7.70
Oxygen .....	0.10	0.10
Ethane .....	36.10	11.50
Nitrogen .....	12.40	71.80
C/A for 'residual gas' .....	1.260	1.250
CO/CO <sub>2</sub> .....	6.14	1.30

We would draw attention to the ratios CO/CO<sub>2</sub> observed in these bulb experiments, the conditions of which precluded the possibility of the independent oxidation of carbon monoxide.

If we consider the experiments in which the combustion proceeded quite normally, that is to say without any secondary decompositions of aldehyde vapours or of the excess of hydrocarbon, we find that for one and the same original mixture of ethane and oxygen the ratio CO/CO<sub>2</sub> in the products is higher the higher the temperature, and therefore also the higher the velocity of the oxidation. Thus, for the original mixtures of equal volumes of ethane and oxygen, at 250° the ratio CO/CO<sub>2</sub> varied between 1.97 and 2.60; at 300°, between 4.1 and 4.9; and in each of the two bulbs at 350° it exceeded 6.0. These observations are quite consistent with the view of the oxidation stages set forth in the introduction of this paper, namely, that carbon monoxide arises in the second stage as the result of the oxidation of acetaldehyde,  $\text{CH}_3\cdot\text{CHO} + \text{O}_2 = \text{CH}_2\text{O} + \text{CO} + \text{H}_2\text{O}$ , as well as during the final oxidation of formaldehyde in the third stage, in which the two simultaneous reactions: (a)  $\text{CH}_2\text{O} + \text{O}_2 = \text{CO}_2 + \text{H}_2\text{O}$ , and (b)  $\text{CH}_2\text{O} + \text{O}_2 + \text{CH}_2\text{O} = 2\text{CO} + 2\text{H}_2\text{O}$ , are concerned.

Again, in the experiments at 300°, in which the proportions of ethane and oxygen in the mixtures employed varied between 2:1 and 1:3.75, the ratio CO/CO<sub>2</sub> in the products naturally decreased with

the higher proportions of oxygen originally present. But it is a significant fact, and one quite explained by our theory of the oxidation stages, that even when the oxygen in the original mixture was more than sufficient to burn all the ethane completely to carbon dioxide and steam, the ratio  $\text{CO}/\text{CO}_2$  in the products did not fall below 1.25.

PART II.—*Experiments with Mixtures of Ethane and Oxygen in the Circulation Apparatus.*

These experiments were undertaken primarily for the identification of the aldehydes, and possibly other condensable or soluble intermediate oxidation products, the formation of which had been proved in the bulb experiments. The circulation apparatus has already been fully described in a previous paper on methane (Trans., 1903, 83, 1074), and is here represented in Fig. 1. Since the experimental method with ethane was, in all essential respects, the same as with methane, we may at once proceed to the discussion of our new results. It was first of all necessary to ascertain whether ethane itself would undergo any change under our experimental conditions. Accordingly we circulated the pure gas in the apparatus for three consecutive days, the temperature of the combustion tube being kept at  $500^\circ$  throughout. A slight expansion (about 4 mm. on 500) was noticed and a subsequent analysis of the gas showed that it contained about 1 per cent. of ethylene and some hydrogen. Thus the values  $\text{C}/\text{A}$  obtained in two explosion analyses of the residual gas after removal of ethylene by means of fuming sulphuric acid were 1.267 and 1.266 respectively. There was no deposition of carbon on the white, porous porcelain with which the combustion tube was packed.

*Identification of Intermediate Products.*—Among the possible soluble and condensable products which could be caught up by the water in the worm E (Fig. 1) were ethyl alcohol, glycol, glyoxal, acet- and formaldehydes, acetic and formic acids. In all our experiments, the liquid had a strong aldehydic smell, reminiscent more of formaldehyde than of acetaldehyde; it reacted strongly with Schiff's reagent, and instantly reduced ammoniacal silver solutions. The liquid was usually quite neutral to litmus, although occasionally it had a distinct acid reaction, due to the presence of small quantities of formic acid, and possibly also of acetic acid. After dilution with an equal volume of water, it was submitted to the following tests.

(1) *The Iodoform Test.*—Ethyl alcohol or acetaldehyde would, of course, give this, but whereas the iodoform precipitated from a dilute acetaldehyde solution is always amorphous, that which separates from dilute solutions of ethyl alcohol is nearly always composed of the characteristic star-like, crystalline aggregates. Occasionally the liquid we

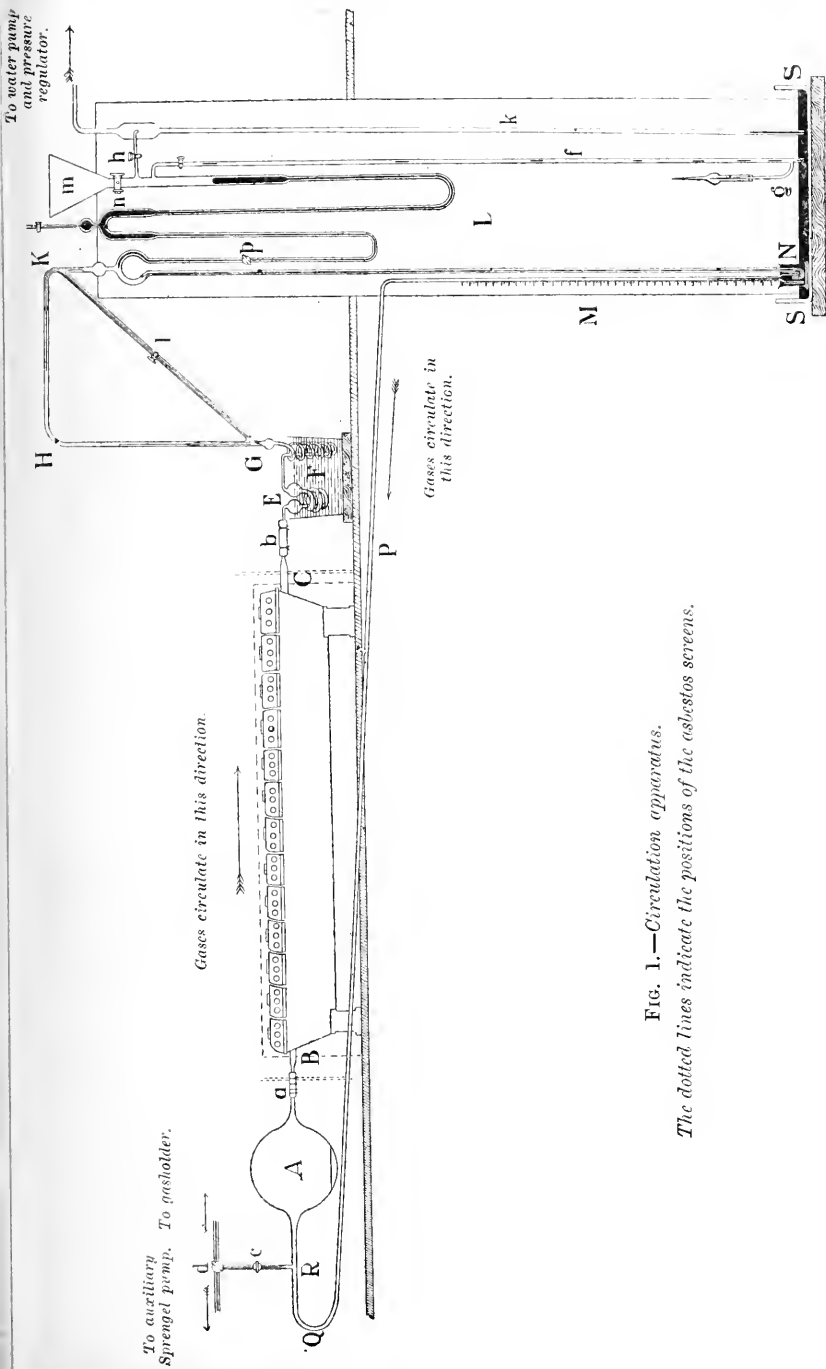


FIG. 1.—Circulation apparatus.

*The dotted lines indicate the positions of the asbestos screens.*

obtained gave amorphous iodoform, but we never got the least indication of a crystalline precipitate. When iodoform was obtained, we repeated the test with another portion of the liquid after it had remained in contact with dilute caustic soda, to polymerise the aldehydes, and subsequently distilled in steam. We never detected any ethyl alcohol in the distillate. In some cases we removed the aldehydes by careful oxidation, at the ordinary temperature, with a slight excess of an ammoniacal silver solution. The liquid was subsequently acidified with dilute sulphuric acid and distilled in steam, but alcohol was never detected in the distillates.

(2) *Reaction with an Acetic Acid Solution of p-Bromophenylhydrazine.*—The aldehydes present could generally be recognised by an examination of the resulting canary-yellow *p*-bromophenylhydrazones. In this way the presence of formaldehyde was always detected, and sometimes that of acetaldehyde also, but there was never the faintest sign of the separation of the deep-red *p*-bromohydrazone of glyoxal.

(3) *Reaction with Hydrogen Sulphide.*—The liquid, without any addition of hydrochloric acid, was saturated with hydrogen sulphide and the test-tube set aside in a warm place for several hours. By this means form- and acet-aldehydes may be distinguished with the greatest certainty (Proc., 1904, 20, 115). We invariably obtained the characteristic white flocculent precipitate of the thio-derivative of formaldehyde.

(4) In some cases, a portion of the liquid was slowly evaporated to dryness in a glass basin over a water-bath. There was never any indication of the separation of glyoxal during the process, or of any solid residue. Once or twice the faintest possible greasy film remained.

Briefly, then, the most prominent and constant intermediate product formed in these experiments was formaldehyde, which was frequently accompanied by smaller proportions of acetaldehyde and, in one or two cases, by traces of formic acid also. There was no direct evidence of the formation of any other intermediate substance such as ethyl alcohol, glycol, or glyoxal.

#### *Details of Experiments.*

Following the plan of our earlier paper on methane (*loc. cit.*, p. 1081—1087), we propose to give: (1) the pressure of the dry nitrogen-free mixture, at the temperature  $t^{\circ}$  of the room, introduced into the cold apparatus, (2) its pressure after the furnace had been lighted and the combustion tube raised to the experimental temperature,  $T^{\circ}$ , (3) the 'corrected' pressures of the dry nitrogen-free gases in the apparatus at successive regular intervals of time, (4) the pressure of the dry nitrogen-free products at the end of the experiment, after the furnace had been turned out and the apparatus

allowed to cool down to the temperature of the room, and (5) the composition of the gaseous products, together with the ratio  $C/A$ , obtained in the explosion analysis of the residual gas after removal of the oxides of carbon, oxygen, and any small amount of ethylene which might be present.

The gases were continuously circulated, day and night, over the hot surface of the porous porcelain in the combustion tube at a constant rate throughout each experiment. This rate was, of course, varied in different experiments, but it may be assumed that the time required for a complete circuit varied between 30 minutes and about 2 hours. This circumstance explains the different rates of oxidation observed with similar mixtures of ethane and oxygen.

The capacity of the whole apparatus was about 1500 c.c., that of the combustion tube was only 75 c.c. Since, however, the temperature of the combustion tube was  $450-500^{\circ}$ , whereas that of the rest of the apparatus was only  $20-25^{\circ}$ , it follows that not more than  $1/50$ th of the total gas in the apparatus was in the heated zone at any one time. But, further, since it has been proved during the research that chemical change is mainly, if not entirely, confined to the layer of gas immediately in contact with the porous surface, it follows that very much less than  $1/50$ th of the total gas was, at any one instant, actually in the sphere of reaction; at the very most not more than  $1/100$ th of the whole gas would be reacting at any given instant. Hence the rates observed in these experiments must be multiplied by at least 100 to give us even an approximate idea of the actual rates of change within the sphere of reaction. It must also be borne in mind that the conditions of these circulation experiments, unlike those of the bulb experiments, admit of the fairly rapid oxidation of free hydrogen as well as of carbon monoxide.

(1) *Experiment with Equal Volumes of Ethane and Oxygen at  $450^{\circ}$ .*

This experiment extended over 10 consecutive days, the speed of circulation was slow, the capillary tubes in GHK (Fig. 1) being in circuit throughout. Mixture E ( $C_2H_6 = 49.7$ ;  $O_2 = 50.3$ ) was used.

Pressure of cold dry nitrogen-free

original mixture at  $18.3^{\circ}$  ..... = 628.4 mm.

Pressure of cold dry nitrogen-free

final products at  $18.3^{\circ}$  ..... = 428.1 mm.

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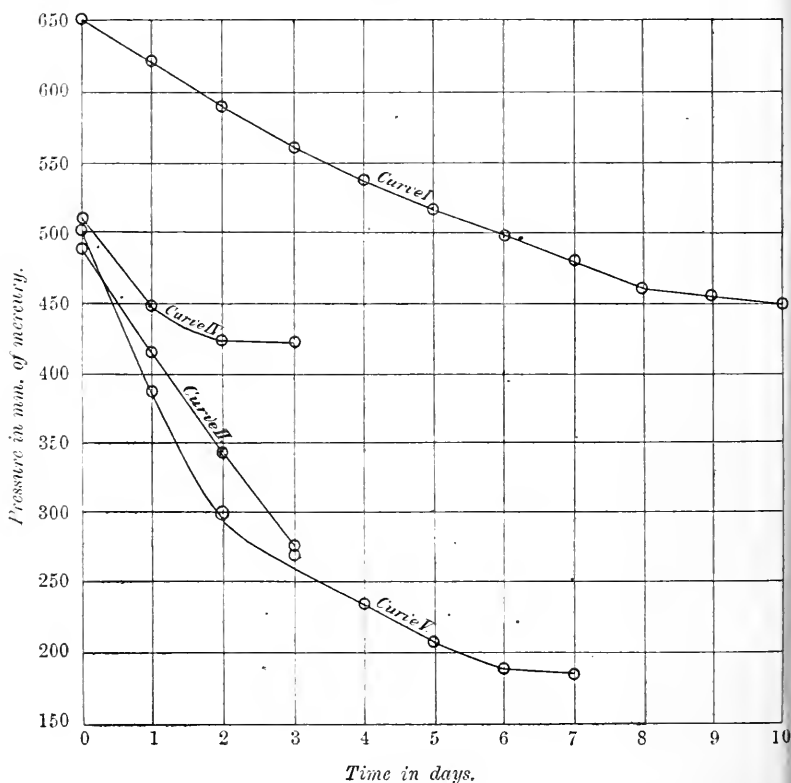
Total pressure fall = 200.3 mm. or 31.9 per cent.

The daily records were as follows :

Days.	Temperature of combustion tube $T^{\circ}$ .	Temperature of globe $t$ .	Corrected pressure of dry nitrogen-free gas.
0	450°	21°	651.3 mm.
1	452	22	622.6 „
2	460	20.8	590.0 „
3	450	20.8	561.2 „
4	447	17.7	538.8 „
5	449	19.0	516.2 „
6	451	19.3	498.7 „
7	440	19.6	480.8 „
8	446	20.0	460.8 „
9	455	18.7	455.1 „
10	450	18.0	449.3 „

The pressure curve for this experiment (Fig. 2, Curve I, ordinates = pressures, abscissæ = time in days) shows that the pressure fall was

FIG. 2.



very regular during the first 8 days, but slackened towards the end of the experiment.

There was no sign of any deposition of carbon on the white porous porcelain during the experiment; this remark applies also to all the other circulation experiments described. The gaseous products still contained some oxygen, considerable quantities of carbon monoxide and dioxide, as well as about 1 per cent. of ethylene and some hydrogen. The ratio C/A for the 'residual gas' was 1.30, which after treatment with palladium fell to 1.25. The mean of three concordant analyses gave the following as the percentage composition of the nitrogen-free gaseous products:

Carbon dioxide ...	19.90	Ethylene .....	1.00
Carbon monoxide..	24.45	Hydrogen.....	3.00
Oxygen .....	4.85	Ethane .....	46.80

The liquid in the worm had an aldehydic odour and reaction, but was quite neutral to litmus. It contained formaldehyde, some acetaldehyde, but no ethyl alcohol.

If we now compare the partial pressures of the ethane and oxygen in the original mixture with those of the various gaseous products at the end of the experiment, we obtain the following numbers:

*Original Mixture.*

Ethane.....	312.4 mm.	Oxygen.....	316.0 mm.
-------------	-----------	-------------	-----------

*Products.*

	mm.		mm.
Carbon dioxide.....	85.2	Ethane .....	200.4
Carbon monoxide.....	104.7	Ethylene .....	4.3
Oxygen.....	20.7	Hydrogen .....	12.8

The 4.3 mm. of ethylene probably arose from a thermal decomposition of a corresponding quantity of ethane; the 12.8 mm. of free hydrogen may be partly ascribed to the same cause, possibly also in part to the thermal decomposition of formaldehyde vapour. The above figures show that 107.7 mm. of ethane had reacted with 295.3 mm. of oxygen, yielding altogether 189.9 mm. of carbon monoxide and dioxide.

(2) *Experiment with Equal Volumes at 500°.*

For this, which, in respect to the amount of aldehydes removed from the sphere of action, is the most remarkable of all our experiments, mixture E ( $C_2H_6 = 49.7$ ;  $O_2 = 50.3$ ) was used.

Pressure of cold dry nitrogen-free

original mixture at 17.5° ..... = 467.6 mm.

Pressure of cold dry nitrogen-free

final products at 17.5°..... = 363.4 mm.

Fall = 204.2 mm., or 43.66 per cent.

The experiment extended over three consecutive days, the temperature of the combustion tube remaining very constant throughout. A rapid rate of circulation was kept up by throwing the capillary tubes in GHK (Fig. 1) out of circuit and allowing the Sprengel pump to work at full speed.

The daily records were as follows :—

Days.	Temperature of combustion tube.	Temperature of globe A.	Corrected pressure of dry nitrogen-free gas.
0 .....	500° .....	21.3° .....	490.7 mm.
1 .....	502 .....	20.8 .....	416.0
2 .....	500 .....	21.7 .....	344.3
3 .....	503 .....	21.5 .....	276.2

The pressure curve for this experiment (Fig. 2, Curve II) is an unbroken straight line.

The liquid in the worm had a distinctly acid reaction and a very strong aldehydic odour. It did not give the iodoform reaction, and therefore contained neither ethyl alcohol nor acetaldehyde. The *p*-bromophenyl-hydrazone prepared from it was identical with that of formaldehyde.

Besides carbon monoxide, carbon dioxide, and unchanged ethane, the gaseous products contained a considerable quantity of oxygen, some hydrogen, and ethylene. The ratio C/A for the residual gas was 1.269, and the percentage composition of the gaseous products was as follows :

	Per cent.		Per cent.
Carbon dioxide.....	20.96	Ethylene .....	2.75
Carbon monoxide ...	16.00	Hydrogen .....	1.30
Oxygen .....	8.00	Ethane.....	51.00

Comparing, again, the partial pressures of the original gases with those of the final products, we have :

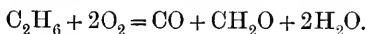
*Original Mixture.*

Ethane..... 232.5 mm.      Oxygen..... 235.1 mm.

*Products.*

	mm.		mm.
Carbon monoxide .....	42.1	Ethylene .....	7.2
Carbon dioxide .....	55.2	Hydrogen .....	3.5
Oxygen .....	21.1	Ethane .....	134.4

These numbers show that whereas 90.7 mm. (that is, 232.5 *minus* 134.4 and 7.2) of ethane had been oxidised during the experiment, the sum of the pressures of carbon monoxide and dioxide in the products only amounted to 97.3 mm., a circumstance which points to a very large formation of formaldehyde according to the empirical equation :



Assuming this to have taken place, then, from the total ethane oxidised and the total oxides of carbon formed, we calculate that no less than 84.1 mm., or 92.7 per cent., of the ethane oxidised appeared in the products as formaldehyde, carbon monoxide (or dioxide), and steam, the remaining 6.6 mm. being completely oxidised to carbon dioxide and steam. Undoubtedly by far the greater part of the carbon dioxide produced in the experiment arose from the independent oxidation of carbon monoxide.

We will now show that the foregoing conclusion agrees very well with the amount of oxygen which actually disappeared during the experiment, namely 214 mm.

84.1 mm. $\text{C}_2\text{H}_6$ oxidised to $\text{CO} + \text{CH}_2\text{O} + 2\text{H}_2\text{O}$	
would require .....	168.2 mm. $\text{O}_2$ .
6.6 mm. $\text{C}_2\text{H}_6$ oxidised to $2\text{CO} + 3\text{H}_2\text{O}$	
would require .....	16.5 mm. „
55.2 mm. $\text{CO}$ oxidised to $\text{CO}_2$ would require ...	27.6 mm. „
	<hr/>
Total.....	212.3 mm.

### (3) *Experiment with Equal Volumes at 500°.*

This is interesting chiefly on account of the extremely rapid rate of oxidation observed, nearly the whole of the oxygen disappearing within 8 hours. Mixture D (ethane = 49.5 ; oxygen = 50.5) was used.

Pressure of cold dry nitrogen-free	
original mixture at 17.8° .....	= 434.6 mm.
Pressure of cold dry nitrogen-free	
final products at 17.8° .....	= 292.0 mm.
	<hr/>

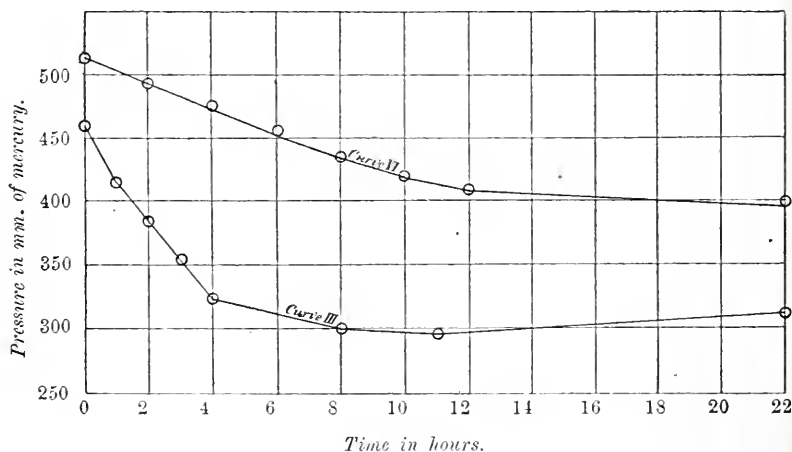
Pressure fall = 142.6 mm., or 32.8 per cent.

The pressure records were as follows :

Time in hours.	Temperature of combustion tube $T^{\circ}$ .	Temperature of the globe $t^{\circ}$ .	Corrected pressure of dry nitrogen-free gases.
0	510°	23.2°	460.3 mm
1	509	25.0	415.0
2	499	25.0	384.0
3	500	26.0	353.8 „
4	503	26.0	324.0 „
8	510	26.5	300.0 „
11	505	26.5	295.4 „
24	504	24.8	310.0 „

The pressure curve for this experiment is shown in Fig. 3, Curve III. It will be observed that a slight expansion occurred after the eleventh

FIG. 3.



hour, the pressure fall up to that time being 35.8 per cent. This expansion must be attributed to the decomposition of acetaldehyde vapour, for there was a considerable accumulation of aldehydes during the experiment, and the gaseous products contained an unusually large quantity of methane.

The liquid in the worm contained acetaldehyde and formaldehyde, but no ethyl alcohol or glyoxal.

The nitrogen-free products contained no free oxygen, and had the following composition:

	Per cent.		Per cent.
Carbon dioxide	35.1	Methane	8.8
Carbon monoxide	10.3	Hydrogen	1.8
Ethylene	2.2	Ethane	41.8

The ratio C/A for the residual gas, after removal of the oxides of carbon and ethylene, was 1.35, which after further treatment with oxidised palladium at 100° was reduced to 1.32.

(4) *Experiment with a Mixture of Ethane and Air at 500°.*

This experiment was performed in the hope that by largely diluting the reacting gases with nitrogen we might possibly detect the formation of ethyl alcohol, and also prevent any secondary decompositions of ethane and aldehyde vapours.

The mixture used contained ethane = 15.80 ; oxygen = 17.65 ; and nitrogen = 66.55 per cent. The experiment extended over three days, but the oxygen had practically all disappeared at the end of the second day.

Pressure of cold dry original mixture at 12.5°	=	467.2 mm.
"      "      "      final products      "      "	=	398.2 mm.
		Fall = 69.0 mm.

This pressure fall is 14.75 per cent., or approximately 44.5 per cent., of the pressure of the original nitrogen-free mixture. The daily records were as follows :

Days.	Temperature of combustion tube T°.	Temperature of globe t°.	Corrected pressure of dry gas at 25°.
0 .....	494° .....	22.0° .....	511.0 mm.
1 .....	500 .....	25.5 .....	449.0 "
2 .....	500 .....	25.0 .....	424.4 "
3 .....	500 .....	25.2 .....	423.4 "

The curve for this experiment is shown in Fig. 2, Curve IV.

The liquid in the worm contained acetaldehyde and formaldehyde, but no ethyl alcohol.

The gaseous products contained only carbon dioxide, carbon monoxide, unchanged ethane, and nitrogen. The ratio C/A for the residual gas was 1.249, showing the entire absence of free hydrogen or methane. Evidently, therefore, dilution with nitrogen had entirely prevented secondary decompositions of ethane and aldehydes. The percentage composition of the gaseous products was :

Carbon dioxide .....	7.00	Ethane .....	10.50
Carbon monoxide .....	4.10	Nitrogen ...	78.4

We calculate that in this experiment about 10 per cent. of the ethane changed appeared in the products as acetaldehyde and steam, 40 per cent. as formaldehyde, carbon monoxide (or dioxide), and steam and that the remainder had been completely burnt to carbon dioxide

and steam. Some of the carbon monoxide liberated in the formation of formaldehyde had undergone independent oxidation.

(5) *Experiment with Mixture of 1 Volume of Ethane to 2 Volumes of Oxygen at 500°.*

For this experiment, which extended over a week, mixture H ( $C_2H_6 = 32.2$ ;  $O_2 = 67.8$ ) was used. The speed of circulation was fairly rapid throughout.

Pressure of the cold dry nitrogen-free original mixture at 17°.....	= 468.9 mm.
Pressure of the cold dry nitrogen-free final products at 17° .....	= 176.8 mm.
	<hr/>
Fall =	292.1 mm.

This pressure fall is 62.3 per cent. of the original pressure. The curve for this experiment (Fig. 2, Curve V) indicates a fairly rapid oxidation during the first two days, followed by a much slower process. The portion of the curve for the latter part of the experiment resembles curves we have obtained for the oxidation of moist carbon monoxide, and it will be seen that carbon dioxide predominated in the gaseous products. The daily records were as follows:

Days.	Temperature of combustion tube $T^\circ$ .	Temperature of globe $t^\circ$ .	Corrected pressure of dry nitrogen-free gas.
0 .....	500° .....	18.5° .....	502.0 mm.
1 .....	499 .....	25.6 .....	387.4 „
2 .....	496 .....	26.8 .....	295.4 „
3 .....	496 .....	26.8 .....	269.9 „
4 .....	484 .....	27.5 .....	235.3 „
5 .....	494 .....	27.8 .....	207.4 „
6 .....	493 .....	27.3 .....	188.1 „
7 .....	487 .....	26.3 .....	185.7 „

The liquid in the worm had a slightly acid reaction; it contained a mere trace of acetaldehyde, but much formaldehyde. The gaseous products contained:

	Per cent.		Per cent.
Carbon dioxide.....	61.40	Ethane.....	13.40
Carbon monoxide.....	23.20	Ethylene ...	1.00
Oxygen.....	0.55	Hydrogen...	0.45

The ratio C/A for the 'residual gas' was 1.273.

Comparing now the partial pressures of the original mixture with those of the gaseous products as under:

*Original Mixture.*

Ethane..... 151.0 mm.      Oxygen..... 317.9 mm.

*Final Products.*

	mm.		mm.
Carbon dioxide.....	108.6	Ethane.....	23.70
Carbon monoxide.....	41.0	Ethylene ...	1.75
Oxygen .....	1.0	Hydrogen...	0.75

We find that whereas 125.5 mm. of ethane underwent oxidation during the experiment, the sum of the pressures of carbon monoxide and dioxide in the products amounted to 149.6 mm. only. We estimate that approximately 80 per cent. of the ethane oxidised appeared in the products as formaldehyde, carbon monoxide (or dioxide), and steam, the remainder being completely burnt to carbon dioxide and steam.

(6) *Experiments with Mixtures of 2 Volumes of Ethane to 1 Volume of Oxygen.*

Having failed to detect any ethyl alcohol among the products of the foregoing experiments, we proceeded to investigate the interaction of mixtures of ethane and oxygen in the ratio 2:1. Since rapid combination is the most favourable condition for the isolation of intermediate products, we circulated these mixtures at top speed, keeping the temperature of the combustion tube at 500°. Under these circumstances, nearly the whole of the oxygen disappeared within 12 hours, a rate hardly inferior to that observed under similar conditions with mixtures of equal volume (Expt. 3, page 717). We also tried experiments at lower temperatures (350° and 400°), but the rate of combination was much slower. In none of these experiments, however, were we able to detect any production of ethyl alcohol. As we need only give the details of one of these experiments, we will select a case in which the products were found to contain a fair quantity of hydrogen. Mixture G was used (ethane = 66.65; O<sub>2</sub> = 33.35), and pressure readings were made every two hours during the early part of the experiment.

Pressure of the cold dry nitrogen-free original mixture at 17°..... = 470.4 mm.

Pressure of the cold dry nitrogen-free final products at 17°..... = 370.0 mm.

---

Fall..... = 100.4 = 21.35 per cent.

The records were as follows :

Hours.	Temperature of the combustion tube $T^{\circ}$	Temperature of the globe $t^{\circ}$	Corrected pressure of dry nitrogen-free gas.
0 .....	480° .....	22.2° .....	514.0 mm.
2 .....	490 .....	25.2 .....	494.0 „
4 .....	493 .....	23.7 .....	476.0 „
6 .....	492 .....	24.2 .....	455.8 „
8 .....	490 .....	24.8 .....	435.0 „
10 .....	492 .....	26.3 .....	419.2 „
12 .....	494 .....	25.9 .....	409.0 „
24 .....	492 .....	26.6 .....	398.8 „

The curve for this experiment is shown in Fig. 3, Curve VI.

The liquid in the worm was quite neutral to litmus and contained acet- and form-aldehydes, but no alcohol. The gaseous products contained :

	Per cent.		Per cent.
Carbon dioxide ...	12.45	Ethane.....	57.10
Carbon monoxide...	15.00	Methane .....	2.30
Oxygen .....	0.30	Hydrogen .....	12.85

The ratio C/A for the residual gas was 1.430, which after removal of hydrogen by means of oxidised palladium sponge at 100°, was reduced to 1.265.

With regard to the other experiments with these mixtures, we may perhaps briefly refer to one in which the combustion tube was packed with fragments of fused quartz instead of the usual porous porcelain, because it illustrates in a striking manner the dependence of the velocity of oxidation on the character of the heated surface employed. In the experiment in question, although the temperature of the combustion tube was maintained at 480—500°, and the pump worked at top speed throughout, the pressure of the gases in the apparatus (measured cold and dry) only fell from 417.5 mm. to 384 mm., or by about 8 per cent., in four days, a rate of reaction only about one-tenth that observed under similar conditions with a catalytic surface of porous porcelain.

### PART III.—*Experiments on the Slow Combustion of Ethyl Alcohol and Acetaldehyde.*

#### A. *Ethyl Alcohol.*

Assuming, for the moment, that the initial stage in the oxidation of ethane involves the formation of ethyl alcohol, the non-occurrence of this compound among the soluble intermediate products in our cir-

culution experiments would be explained if it could be shown that, under similar conditions, alcohol reacts with oxygen much more rapidly than does ethane itself. It was also important to ascertain whether or not the intermediate stages of the oxidation of alcohol are of the same character and sequence as those of ethane, namely: (1), formation of acetaldehyde and steam, and (2) formation of carbon monoxide, formaldehyde, and steam.

As it was not feasible to use the circulation apparatus for these experiments, we set up a special apparatus in which air or oxygen could be passed at a constant rate (about  $1\frac{1}{2}$  litres per hour) through (1) a series of glass worms containing pure ethyl alcohol kept at a definite temperature ( $t^\circ$ ) in a large water-bath, (2) a combustion tube packed with porous porcelain, of the same dimensions as the tube used in the circulation apparatus, heated to a constant temperature ( $T^\circ$ ), and (3) two worms containing water, and externally cooled by water for the removal of soluble intermediate products. Arrangements were also made for the collection of samples of the exit gases. The conditions of these experiments were therefore fairly comparable with those of the ethane circulation experiments, except that of course in the latter the reacting gases passed many times over the heated surface. Our object was to ascertain the limiting proportion of alcohol vapour which could enter the combustion tube without any of it surviving a single passage over the heated surface.

The vapour pressures of alcohol at the various saturation temperatures employed are as follows:

$t.$	$10^\circ.$	$20^\circ.$	$30^\circ.$	$40^\circ.$	$50^\circ.$
$p.$	24.2	44.5	78.5	134.0	220.0 mm.

(a) *Experiments with Air.*

(i) With the furnace at  $300^\circ$ , traces of alcohol appeared in the products with a saturation temperature of  $20^\circ$ . The liquid in the worm contained acetaldehyde but no formaldehyde. The exit gases contained a trace of carbon dioxide and 18.7 per cent. of oxygen.

(ii) With the furnace at  $350^\circ$ , no alcohol survived the passage through the combustion tube with a saturation temperature of  $20^\circ$ , but it appeared in the exit gases with a saturation temperature of  $30^\circ$ . The products contained much acetaldehyde and also some formaldehyde, and the gases from one experiment (saturation temperature  $20^\circ$ ) contained:  $\text{CO}_2 = 1.9$ ;  $\text{CO} = 2.8$ ; and  $\text{O}_2 = 13.8$  per cent.

(iii) With the furnace at  $500^\circ$ , no alcohol survived a single passage over the heated surface at all saturation temperatures under  $35^\circ$ , but it appeared in the exit gases when the saturation temperature was  $40^\circ$ . The liquid in the worms now had a faintly acid reaction,

and contained both acetaldehyde and formaldehyde. The gaseous products from one experiment (saturation temperature =  $40^{\circ}$ ) contained  $\text{CO}_2 = 5.5$ ;  $\text{CO} = 12.0$ ;  $\text{O}_2 = \text{nil}$ ;  $\text{C}_2\text{H}_4 = 1.5$ ;  $\text{CH}_4 = 4.0$  per cent.

All the foregoing oxidation rates are far in excess of those observed with ethane at corresponding temperatures in the circulation apparatus.

(b) *With a Mixture of Oxygen = 48.6 per cent. and Nitrogen = 51.4 per cent.*

With the furnace at  $425^{\circ}$ , the ingoing gas was sometimes saturated at  $50^{\circ}$  even without alcohol appearing in the exit gases. The liquid in the worms, which was neutral to litmus, contained acetaldehyde and much formaldehyde, but no glyoxal. The gaseous products from one experiment (saturation temperature =  $40^{\circ}$ ) contained:  $\text{CO}_2 = 3.1$ ;  $\text{CO} = 8.5$ ;  $\text{O}_2 = 35.1$ ; and  $\text{CH}_4 = 0.8$  per cent.

(c) *With 95 per cent. Oxygen.*

(i) With the furnace at  $450^{\circ}$ , and the gas saturated at  $30^{\circ}$ , no alcohol escaped from the combustion tube. The liquid in the worms had a faintly acid reaction; it contained acetaldehyde and much formaldehyde, but no glyoxal. The gaseous products contained:  $\text{CO}_2 = 3.7$ ;  $\text{CO} = 13.0$ ;  $\text{O}_2 = 77.0$  per cent.

(ii) With the furnace at  $450^{\circ}$ , and the gas saturated at  $50^{\circ}$ , a mere trace of the alcohol vapour survived the passage over the heated surface. The liquid in the worms, which had a distinctly acid reaction, contained acetaldehyde and formaldehyde, but no glyoxal. The gaseous products contained:  $\text{CO}_2 = 6.0$ ;  $\text{CO} = 12.8$ ;  $\text{O}_2 = 76.4$ ;  $\text{C}_2\text{H}_4 = 0.3$ ;  $\text{CH}_4 = 0.3$ ;  $\text{N}_2 = 4.2$  per cent.

The conclusions, therefore, to be drawn from these experiments are:

(1) That ethyl alcohol reacts with oxygen far more rapidly than does ethane itself under similar conditions.

(2) That its oxidation stages, like those of ethane, involve the successive formation of (a) acetaldehyde and (b) formaldehyde, together with considerable quantities of carbon monoxide.

### B. Acetaldehyde.

It finally remained to show that acetaldehyde and oxygen react in our circulation apparatus forming formaldehyde in conformity with the views expressed in the earlier part of this paper. The experimental method was as follows.

Just sufficient water was introduced into the globe of the apparatus to keep its inner surface wet during the experiment; about 20 c.c. of

water were put into the worm. The apparatus was then completely exhausted of air, the furnace lighted, and the combustion tube raised to the desired experimental temperature. Moist oxygen was then admitted into the apparatus until the manometer recorded a pressure of about 250 mm. The oxygen supply having been cut off, connection was made with a small distillation flask containing acetaldehyde; the air in the flask had been previously completely expelled by the vapour of the boiling liquid. The vapour of the acetaldehyde was then slowly admitted to the apparatus until the manometer indicated a further fall of about 300 mm.

The mixture of aldehyde vapour and oxygen was then rapidly circulated, pressure records being taken at frequent intervals. Finally, a sample of the gaseous products was withdrawn and analysed after any aldehyde vapours present had been polymerised and removed by contact with a layer of pure sulphuric acid. The liquid in the worm was also carefully examined for formaldehyde.

### 1st Experiment.

Pressure of oxygen (dry) originally admitted	=	250 mm.
„ „ aldehyde vapour „ „	=	291 „
		—
Total	=	541 „

There was a fairly rapid pressure fall in the apparatus during the first hour and a half, but during the next hour hardly any further fall was observed. This stationary period was succeeded by a very gradual rise in pressure, which was maintained on continuing the circulation overnight.

The records obtained were as follows:

Time in hours.	Temperature of combustion tube $T^{\circ}$ .	Corrected pressure for dry mixture.
0 .....	451° .....	541 mm.
1½ .....	460 .....	462 „
2½ .....	461 .....	462 „
3½ .....	459 .....	471 „
5½ .....	460 .....	474 „
7½ .....	464 .....	481 „
21½ .....	474 .....	504 „

The liquid in the worm was nearly neutral to litmus and contained much formaldehyde; during the experiment, also, a small quantity of a white solid, apparently paraformaldehyde, appeared on the surface of the globe A.

The gaseous products had the following percentage composition :

Carbon dioxide.....	23·5	Methane.....	23·35
Carbon monoxide.....	47·1	Hydrogen.....	4·45
Oxygen.....	nil	Nitrogen... ..	1·60

From the large proportion of methane present it is evident that a considerable amount of the acetaldehyde had undergone a purely thermal decomposition during the experiment.

### *2nd Experiment.*

Pressure of aldehyde vapour introduced	=	293 mm.
„ „ oxygen (dry)	=	233 „
		<hr/>
		526 „

The mixture was circulated for 24 hours ; at first, a rapid fall of pressure was observed, followed by a slow and continuous rise. The final pressure of the dry products was 450 mm.

The liquid in the worm again contained much formaldehyde, and the gaseous products had nearly the same composition as those obtained in the first experiment, namely :

	Per cent.		Per cent.
Carbon dioxide.....	24·6	Methane.....	19·0
Carbon monoxide.....	51·4	Hydrogen.....	4·1
Nitrogen .....	0·9		

### *3rd Experiment.*

In this experiment, pressure records were taken every 15 minutes, and the furnace was turned out as soon as the pressure fall had ceased.

Pressure of aldehyde vapour introduced	=	283 mm.
„ „ oxygen (dry)	=	265 „
		<hr/>
		548 „

The records were as follows :

Time in minutes.	Temperature of combustion tube T°.	Corrected pressure of dry mixture.
0 .....	479° .....	548 mm.
15 .....	479 .....	513 „
30 .....	479 .....	496 „
45 .....	479 .....	490 „
60 .....	479 .....	490 „

The liquid in the worm again contained formaldehyde, and the gaseous products, which contained no free oxygen, had the following composition :

	Per cent.		Per cent.
Carbon dioxide.....	34·35	Methane.....	15·35
Carbon monoxide... ..	48·25	Hydrogen .....	1·00
Nitrogen.....	1·05		

The indications obtained in the above experiments of the thermal decomposition of acetaldehyde vapour in contact with the heated surface led us to try the effect of circulating acetaldehyde vapour itself in our apparatus. We have already stated (p. 695) that acetaldehyde, when heated in borosilicate bulbs at 300—350°, undergoes simple decomposition in accordance with the equation  $\text{CH}_3\cdot\text{CHO} = \text{CH}_4 + \text{CO}$ . The changes which occur when the aldehyde vapour is passed over a surface of porous porcelain maintained at 450° are, however, of a more complex character. Some polymerisation or condensation takes place, and the condensed molecules undergo thermal decomposition as well as those of the simpler acetaldehyde vapour. The gaseous products from one experiment, for instance, contained:  $\text{CO}_2 = 58\cdot5$ ;  $\text{CO} = 6\cdot7$ ;  $\text{C}_2\text{H}_4 = 0\cdot7$ ;  $\text{CH}_4 = 31\cdot0$ ; and  $\text{H}_2 = 3\cdot1$  per cent.

When, however, the aldehyde vapour was largely diluted with inert nitrogen, relatively much larger proportions of methane were formed. The whole subject of the thermal decomposition of these aldehyde vapours, which requires careful working out in detail, is now being taken in hand.

Experiments are also being carried out in these laboratories on (1) the slow combustion of acetylene and ethylene, (2) the action of ozone on the simpler hydrocarbons at the ordinary temperature, and (3) the union of hydrogen and oxygen, and of carbon monoxide and oxygen, in contact with heated surfaces of porous porcelain.

In conclusion, we desire to tender our best thanks to the Government Grant Committee of the Royal Society for repeated grants towards the expenses of this and allied researches.

THE OWENS COLLEGE,  
MANCHESTER.

LXXIII.—*Studies in the Tetrahydronaphthalene Series.*  
*Part II. Halogen Derivatives of ar-Tetrahydro- $\beta$ -naphthylamine.*

By CLARENCE SMITH, D.Sc.

WHEN  $\beta$ -naphthylamine is reduced by sodium and amyl alcohol, two isomeric tetrahydronaphthylamines are produced (Bamberger and Müller, *Ber.*, 1888, 21, 847, 1112), and it has been shown that one of these, namely, *ar*-tetrahydro- $\beta$ -naphthylamine has lost its naphthalenoid characteristics, and behaves like a benzenoid amine in forming stable diazoamines (Trans., 1902, 81, 900).

The benzenoid character of *ar*-tetrahydro- $\beta$ -naphthylamine is further exemplified by its behaviour towards the halogens. The hydrogen atom in the  $\alpha$ -position, which so readily undergoes substitution in  $\beta$ -naphthylamine, has to a great extent lost its reactivity in the tetrahydrogenated base, and is now comparable with hydrogen in the ortho-position with respect to the amino-radicle in a benzenoid amine.

Thus it is found that with one molecular proportion of bromine at the ordinary temperature, acetyl-*ar*-tetrahydro- $\beta$ -naphthylamine forms two monobromo-compounds, in one of which the halogen atom has entered the ortho-position with respect to the aminic nitrogen, whilst in the other the meta-position is assumed. With aceto- $\beta$ -naphthalide, however, the reactive hydrogen atom in the  $\alpha$ -position alone undergoes displacement, resulting in the production of aceto-1-chloro- $\beta$ -naphthalide (Cleve, *Ber.*, 1887, 20, 1989) or of aceto-1-bromo- $\beta$ -naphthalide (Cosiner, *Ber.*, 1881, 14, 59), even when the halogen is employed in excess.

The positions taken up by the bromine atoms in the two bromo-*ar*-tetrahydro- $\beta$ -naphthylamines were determined by eliminating the amino-radicle with the formation in both cases of 1-bromotetrahydronaphthalene,\* a compound which was also prepared directly from *ar*-tetrahydro- $\alpha$ -naphthylamine by the Sandmeyer reaction.

\* [In this and the two succeeding papers, the orientation of the substituent radicles (other than amidogen) in the tetrahydronaphthalene derivatives under discussion is denoted by numerals, the numbering being commenced in the aromatic ring in accordance with the following scheme :



—EDITOR.]

## EXPERIMENTAL.

The following bromotetrahydronaphthalenes were prepared in order to assist in determining the positions taken up by other substituent radicles in the tetrahydronaphthalene series.

*1-Bromotetrahydronaphthalene, C<sub>10</sub>H<sub>11</sub>Br.*

A paste consisting of 30 grams (1 mol.) of *ar*-tetrahydro- $\alpha$ -naphthylamine, 100 c.c. ( $2\frac{1}{2}$  mols.) of hydrobromic acid (sp. gr. 1.308), and 50 c.c. of water was diazotised at 2—3° with the requisite amount of sodium nitrite, the clear yellow solution of the diazonium bromide being then added slowly to a solution of cuprous bromide. With each addition of the diazonium salt, an orange-red coloration was produced, which rapidly disappeared on shaking. The contents of the flask were then distilled in steam, and *1-bromotetrahydronaphthalene* collected in the receiver as a yellow oil together with a considerable quantity of *ar*-tetrahydro- $\alpha$ -naphthol.

Sodium hydroxide was added to the distillate in order to dissolve the phenolic substance; the insoluble oil was extracted with ether, the extract being washed with water, dried over calcium chloride, and then distilled. The main portion distilled between 250° and 260° under 751 mm. pressure, and on rectification a fraction was obtained which boiled at 255—257°, and was analysed with the following result.

0.3013 gave 0.2668 AgBr. Br = 37.68.

C<sub>10</sub>H<sub>11</sub>Br requires Br = 37.91 per cent.

*1-Bromotetrahydronaphthalene* is a colourless, refractive liquid, with an aromatic odour resembling that of the halogenated benzene compounds; it darkens in colour until finally it becomes almost black. It is easily soluble in organic solvents and volatile in steam.

*2-Bromotetrahydronaphthalene, C<sub>10</sub>H<sub>11</sub>Br.*

This compound, which was obtained from *ar*-tetrahydro- $\beta$ -naphthylamine by the method described in the preceding experiment, is a colourless, highly refractive liquid which boils between 238° and 239° under 758 mm. pressure; it closely resembles the  $\alpha$ -compound in appearance, odour, and solubility.

0.2667 gave 0.2355 AgBr. Br = 37.57.

C<sub>10</sub>H<sub>11</sub>Br requires Br = 37.91 per cent.

*Action of Bromine on Acetyl-ar-tetrahydro-β-naphthylamine.*

Bromination of the acetyl compound proceeds readily at the ordinary temperature, but the best yield of *acetylbromo-ar-tetrahydro-β-naphthylamine* was obtained under the following conditions.

A solution of 5 grams of the acetylated amine in 15 grams of glacial acetic acid was maintained at 50—60°, while 4 grams of bromine dissolved in 10 grams of the same solvent were slowly added. After half an hour, during which time hydrobromic acid was evolved copiously, the mixture was heated on the water-bath for a few minutes and allowed to cool. The solid which had separated was filtered, washed with acetic acid, and crystallised from alcohol. After several crystallisations from this solvent, the substance was obtained in colourless, octahedral crystals which melted at 125·5°.

0·3220 gave 0·2264 AgBr. Br = 29·92.

$C_{12}H_{14}ONBr$  requires Br = 29·85 per cent.

The substance, which is, therefore, an *acetylbromo-ar-tetrahydro-β-naphthylamine*, dissolves only sparingly in light petroleum or cold alcohol, and is moderately soluble in hot glacial acetic acid, ethyl acetate, or hot alcohol.

The mother-liquor from which the preceding acetyl derivative had been separated was diluted with water, whereby a solid substance was precipitated. After several crystallisations from alcohol, the compound was obtained in colourless needles melting at 151°.

0·1632 gave 0·1146 AgBr. Br = 29·88.

$C_{12}H_{14}ONBr$  requires Br = 29·85 per cent.

This second *acetylbromo-ar-tetrahydro-β-naphthylamine* differs markedly from the first in its solubilities. It dissolves very easily in acetic acid, acetone, ethyl acetate, or alcohol, and is moderately soluble in light petroleum.

The yields of the two brominated acetyl derivatives melting at 125·5° and 151° are respectively 82 per cent. and 12 per cent. of the theoretical.

*The Isomeric Bromo-ar-tetrahydro-β-naphthylamines.*

From the two brominated acetyl derivatives, the bases were obtained in the usual way. Ten grams of *acetylbromo-ar-tetrahydro-β-naphthylamine* (m. p. 125·5°) were heated for thirty minutes on the water-bath with 15 c.c. of alcohol and 10 c.c. of concentrated hydrochloric acid. The *hydrochloride* of the base was obtained in long, white

needles which are moderately soluble in hot water, undergoing partial dissociation. The free *base* was precipitated, by the addition of sodium hydroxide, as an oil which slowly solidified. The dried solid, when crystallised from light petroleum, separated in colourless, silky needles melting at  $52^{\circ}$ .

The base is easily soluble in alcohol, ethyl acetate, or acetone, moderately so in light petroleum or hot water, and almost insoluble in cold water; it is easily volatile in steam.

0.3153 gave 0.2621 AgBr. Br = 35.38.

$C_{10}H_{12}NBr$  requires Br = 35.39 per cent.

The brominated acetyl derivative melting at  $151^{\circ}$  does not hydrolyse as readily as the isomeric compound.

Ten grams of the substance melting at  $151^{\circ}$  were heated for two hours in alcoholic solution with strong hydrochloric acid. The hydrochloride separated from the cold liquid in long, prismatic needles. The free *base* was obtained as an oil by adding sodium hydroxide to the aqueous solution of the hydrochloride. The oil slowly solidified, and the dried solid, when crystallised from light petroleum, separated in colourless needles which melted at  $52^{\circ}$ . The base is not volatile in steam; it dissolves readily in alcohol, chloroform, or ethyl acetate, but is only moderately soluble in light petroleum or hot water.

0.1249 gave 6.8 c.c. moist nitrogen at  $14.5^{\circ}$  and 765 mm. N = 6.43.

0.2871 „ 0.2394 AgBr. Br = 35.49.

$C_{10}H_{12}NBr$  requires Br = 35.49. N = 6.19 per cent.

Although these isomeric brominated bases resemble one another so closely in their crystalline forms and melting points, they are proved to be different compounds, not only because they yield different hydrochlorides and acetyl derivatives, but also from the fact that a mixture of equal quantities of the bases forms an oil at the ordinary temperature.

#### *1-Bromotetrahydronaphthalene Derived from the Two Brominated Bases.*

The two bromo-*ar*-tetrahydro- $\beta$ -naphthylamines are both oxidised to adipic acid by alkaline permanganate, a result which shows that the bromine atom is not situated in the hydrogenated nucleus. In order to determine the position of the halogen, the amino-group was eliminated from the brominated bases with the production of 1-bromotetrahydronaphthalene in both cases. Hence the bromine atoms in the two brominated bases must be situated in the positions 1 and 4 respectively with reference to the amino-group.

Ten grams of the hydrochloride of bromo-*ar*-tetrahydro- $\beta$ -naphthyl-

amine (m. p.  $52.5^{\circ}$ ) were suspended in 15 c.c. of cold hydrochloric acid and diluted with 30 c.c. of water, and diazotised with the requisite amount of sodium nitrite. The solution of the diazonium salt was then poured into an ice-cold solution of 20 grams of sodium hydroxide in 60 c.c. of water. To the mixture cooled by ice was added, slowly and in small quantities at a time, a concentrated solution of stannous chloride (40 grams) in sodium hydroxide. When the whole of the reducing agent had been added, and the evolution of nitrogen had ceased, the product was distilled in steam.

The yellow oil in the distillate was extracted with ether, washed with dilute sulphuric acid and water, and dried over calcium chloride. On distillation, after removing the solvent, a colourless oil passed over between  $255^{\circ}$  and  $260^{\circ}$  under 764 mm. pressure. By redistillation, the main portion was collected between  $258^{\circ}$  and  $259^{\circ}$ , and was thus recognised as 1-bromotetrahydronaphthalene (b. p.  $255-257^{\circ}/751$  mm.).

0.3179 gave 0.2813 AgBr. Br = 37.65.

$C_{10}H_{11}Br$  requires Br = 37.91 per cent.

A similar experiment was performed on the bromo-*ar*-tetrahydro- $\beta$ -naphthylamine, melting at  $52^{\circ}$ .

The colourless oil ultimately obtained distilled between  $254^{\circ}$  and  $256^{\circ}$  under 758 mm.

0.2863 gave 0.2528 AgBr. Br = 37.58.

$C_{10}H_{11}Br$  requires Br = 37.91 per cent.

The compound was identical with 1-bromotetrahydronaphthalene in its other physical properties.

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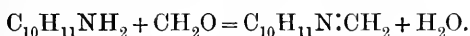
LXXIV<sup>\*</sup>.—*Studies in the Tetrahydronaphthalene Series.*  
*Part III. Reaction between ar-Tetrahydro- $\beta$ -naphthylamine and Formaldehyde.*

By CLARENCE SMITH, D.Sc.

THE course of the reaction between formaldehyde and  $\beta$ -naphthylamine differs markedly from that which occurs between this aldehyde and the primary benzenoid amines. In the former case, the final product is chiefly naphthacridine (Reed, *J. pr. Chem.*, 1886, 35, 314; Morgan, *Trans.*, 1898, 73, 536). With benzenoid amines, anhydro-bases of the

type  $R \cdot N : CH_2$  are obtained ; these substances, which exist generally in the bimolecular or trimolecular state, are unsaturated compounds, forming additional products with hydrogen, the halogens, and hydrogen cyanide, and are readily hydrolysed into their generators by dilute acids (von Miller and Plöchl, *Ber.*, 1892, 25, 2020 ; Bischoff, *Ber.*, 1898, 31, 3251).

*ar*-Tetrahydro- $\beta$ -naphthylamine exhibits its benzenoid character when submitted to the action of formaldehyde. In consequence of the decreased reactivity of the hydrogen atom in the  $\alpha$ -position in *ar*-tetrahydro- $\beta$ -naphthylamine, there is no tendency towards the production of an acridine, and an anhydro-base quite analogous to methyleneaniline is formed in accordance with the equation :



Von Miller and Plöchl (*loc. cit.*) obtained two substances by the action of formaldehyde on aniline ; one of these was methyleneaniline in the trimolecular state, the other they were unable to identify, but concluded that it was a higher polymeride of methyleneaniline, since both substances gave the same reactions.

Two substances are likewise produced in the reaction between *ar*-tetrahydro- $\beta$ -naphthylamine and formaldehyde and one of these is methylene-*ar*-tetrahydro- $\beta$ -naphthylamine in the trimolecular state. In this case, however, there is no doubt that the other substance is also a polymeride of the anhydro-base, for not only do both substances exhibit the same reactions, but each can be changed into the other by the aid of solvents. The trimolecular form is partially changed into the higher polymeride by evaporating its solution in boiling alcohol ; the higher polymeride is changed almost entirely into the crystalline trimolecular form by dissolving it in boiling benzene. Methylene-*ar*-tetrahydro- $\beta$ -naphthylamine is an unsaturated substance ; it forms an unstable additive compound with bromine, and by reduction with sodium and amyl alcohol yields methyl-*ar*-tetrahydro- $\beta$ -naphthylamine, which possesses properties resembling those of the corresponding ethyl base.

#### EXPERIMENTAL.

##### *Methylene-ar-tetrahydro- $\beta$ -naphthylamine*, $(C_{10}H_{11}N : CH_2)_3$ .

Ten grams of fused *ar*-tetrahydro- $\beta$ -naphthylamine were mixed with sufficient alcohol to keep the mixture liquid at the ordinary temperature, and 9 grams of a 35 per cent. formaldehyde solution were then slowly added. Towards the end of the operation, a heavy oil suddenly separated and the temperature rose considerably. The remainder of the formaldehyde was added and the mixture was allowed to remain for

three hours. The clear, supernatant liquid containing only formaldehyde was decanted, and the extremely viscid pink product, which had a waxy appearance, was well washed with water and dried. The greater part of the substance dissolved in boiling acetone, the residue consisting of 2 grams of a white, amorphous powder (B). Eight grams of colourless needles (A) crystallised from the solution.

(A) By successive crystallisation from acetone and light petroleum, this substance was obtained as a felted mass of white needles which melted at  $121^{\circ}$ ; it was easily soluble in benzene, chloroform, or acetone, but only sparingly so in light petroleum. By gently warming the substance with glacial acetic acid, an intense blood-red coloration was produced.

0.2128 gave 0.6250  $\text{CO}_2$  and 0.1567  $\text{H}_2\text{O}$ .  $\text{C} = 83.18$ ;  $\text{H} = 8.18$ .

0.1771 „ 0.5375  $\text{CO}_2$  „ 0.1276  $\text{H}_2\text{O}$ .  $\text{C} = 82.77$ ;  $\text{H} = 8.01$ .

0.1753 „ 13.2 c.c. moist nitrogen at  $16^{\circ}$  and 767 mm.  $\text{N} = 8.86$ .

0.1116 „ 8.7 „ „ „ 748 „  $\text{N} = 8.94$ .

$\text{C}_{11}\text{H}_{13}\text{N}$  requires  $\text{C} = 83.02$ ;  $\text{H} = 8.18$ ;  $\text{N} = 8.80$  per cent.

The compound possesses properties analogous to those of methyleneaniline; it is unsaturated, forming an unstable perbromide, and is reduced to methyl-*ar*-tetrahydro- $\beta$ -naphthylamine; it does not form a benzoyl derivative, and is decomposed by dilute acids, *ar*-tetrahydro- $\beta$ -naphthylamine being regenerated.

The determination of the molecular weight by the cryoscopic method gave results which indicate that the substance, like the analogous methyleneaniline, exists in the trimolecular state.

0.2102 in 16.361 benzene gave  $\Delta t = 0.165^{\circ}$ .  $\text{M. W.} = 413$ .

0.1173 „ 13.362 „ „ 0.116 $^{\circ}$ .  $\text{M. W.} = 401$ .

$(\text{C}_{10}\text{H}_{11}\text{N}:\text{CH}_2)_3$  requires  $\text{M. W.} = 477$ .

$(\text{C}_{10}\text{H}_{11}\text{N}:\text{CH}_2)_2$  „  $\text{M. W.} = 318$ .

(B) The amorphous, white powder darkens at  $156^{\circ}$  and fuses at  $164$ – $165^{\circ}$ ; it is almost insoluble in acetone, light petroleum, or benzene, but dissolves in hot alcohol. With warm acetic acid, it gives a blood-red coloration.

0.1877 gave 0.5700  $\text{CO}_2$  and 0.1365  $\text{H}_2\text{O}$ .  $\text{C} = 82.83$ ;  $\text{H} = 8.08$ .

0.2011 „ 0.6100  $\text{CO}_2$  „ 0.1487  $\text{H}_2\text{O}$ .  $\text{C} = 82.73$ ;  $\text{H} = 8.21$ .

0.2676 „ 21 c.c. moist nitrogen at  $16^{\circ}$  and 766 mm.  $\text{N} = 9.22$ .

$\text{C}_{11}\text{H}_{13}\text{N}$  requires  $\text{C} = 83.02$ ;  $\text{H} = 8.18$ ;  $\text{N} = 8.80$  per cent.

It appears, therefore, that the substance B is a polymeric form of methylene-*ar*-tetrahydro- $\beta$ -naphthylamine.

*Action of Solvents on Compounds A and B.*—The attempt to determine the molecular weight of compound B gave the following results.

At the ordinary temperature, 0.0521 gram of this compound was insoluble in about 18 grams of benzene, but dissolved at  $40^{\circ}$ ; the clear solution did not yield the original substance, and the depression of the freezing point of 18.451 grams of benzene was  $0.035^{\circ}$ , corresponding with a molecular weight of 427.

In another experiment, 0.0976 gram dissolved at  $40^{\circ}$  depressed the freezing point of 27.27 grams of benzene by  $0.042^{\circ}$ , corresponding with a molecular weight of 421.

As the compound B, which is insoluble in cold benzene, dissolves in the warm solvent at  $40^{\circ}$  and is not reprecipitated on cooling the solution, and as the observed molecular weight of the dissolved substance is about 420, these results seem to indicate that this polymeride has been converted almost entirely into the trimolecular form  $(C_{10}H_{11}N:CH_2)_3$ .

To verify this conclusion, 2 grams of the compound B were dissolved in boiling benzene and the solution concentrated, when white needles separated, which, after crystallisation from acetone, melted at  $121^{\circ}$  and were identical with the compound A.

On the other hand, when the substance A was dissolved in boiling alcohol and the solvent allowed to evaporate, the oil, which separated slowly, solidified. This solid was boiled with 50 c.c. of acetone, and the white, amorphous, insoluble residue, when washed with acetone and dried, melted at  $164-165^{\circ}$  and was identical with the substance B.

An intimate mixture of the two substances A and B melts in a remarkable manner. Fusion does not take place until the melting point ( $121^{\circ}$ ) of A is reached; then partial fusion occurs, but the mixture does not become wholly liquid until the melting point ( $164-165^{\circ}$ ) of the substance B is attained.

*Methyl-ar-tetrahydro- $\beta$ -naphthylamine*,  $C_{10}H_{11}\cdot NH\cdot CH_3$ .—Twenty grams of methylene-ar-tetrahydro- $\beta$ -naphthylamine, dissolved in 400 c.c. of boiling amyl alcohol, were reduced by means of 50 grams of sodium until a sample of the solution did not turn red on the addition of dilute hydrochloric acid. The liquid was poured into 400 c.c. of water, the aqueous solution of sodium hydroxide drawn off, the alcoholic liquid acidified with hydrochloric acid, and evaporated to 50 c.c. and cooled. The hydrochloride which separated from the cold solution was collected and washed with ether until colourless. The base was liberated by sodium hydroxide, extracted with ether and dried over solid caustic potash. After removal of the solvent, an oil remained which boiled at  $267.5^{\circ}$  under 210 mm. pressure. The distillate was a colourless, almost odourless, highly refractive oily liquid, which turned brown on exposure to the air. It dissolves easily in organic solvents, is sparingly soluble in hot water, and possesses feebly basic properties.

0.2668 gave 0.8051  $\text{CO}_2$  and 0.2317  $\text{H}_2\text{O}$ .  $\text{C} = 82.30$  ;  $\text{H} = 9.65$ .  
 0.2284 „ 16 c.c. moist nitrogen at  $18^\circ$  and 778 mm.  $\text{N} = 8.29$ .  
 $\text{C}_{11}\text{H}_{15}\text{N}$  requires  $\text{C} = 81.99$  ;  $\text{H} = 9.32$  ;  $\text{N} = 8.69$  per cent.

The *nitrate*,  $\text{C}_{10}\text{H}_{11}\cdot\text{NH}\cdot\text{CH}_3\cdot\text{HNO}_3$ , is obtained by shaking an ethereal solution of the base with dilute nitric acid ; it separates in colourless needles, which are easily soluble in cold water.

The *hydrochloride*,  $\text{C}_{10}\text{H}_{11}\cdot\text{NH}\cdot\text{CH}_3\cdot\text{HCl}$ , produced by adding dilute hydrochloric acid to the base suspended in water, separates in white, sparingly soluble needles.

The *nitrosoamine*,  $\text{C}_{10}\text{H}_{11}\cdot\text{N}(\text{CH}_3)\cdot\text{NO}$ , is prepared by adding the requisite amount of sodium nitrite to an acidified solution of the hydrochloride. The yellow oil when extracted with ether and dried over calcium chloride, gives Liebermann's reaction, developing an intense red coloration in the acid solution, which changes to greenish-blue on the addition of sodium hydroxide.

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## LXXV.—*A Study of the Substitution Products of ar-Tetrahydro- $\alpha$ -naphthylamine. 4-Bromotetrahydro- $\alpha$ -naphthylamine and ar-Tetrahydro- $\alpha$ -naphthylamine-4-sulphonic Acid.*

By GILBERT THOMAS MORGAN, FRANCES MARY GORE MICKLETHWAIT,  
 and HERBERT BEN WINFIELD.

*ar*-TETRAHYDRO- $\alpha$ -NAPHTHYLAMINE, originally obtained by Bamberger and Althausse (*Ber.*, 1888, 21, 1786) on reducing  $\alpha$ -naphthylamine with sodium and boiling amyl alcohol, was shown by these investigators to have the general properties of an aromatic amine, and in certain respects to be more closely allied to aniline and its homologues (more particularly *o*-2-xylidine) than to the original naphthalenoid amine (Bamberger, *Annalen*, 1890, 257, 11). Nevertheless, the tetrahydrogenated base resembles  $\alpha$ -naphthylamine in the facility with which it interacts with diazonium salts to yield aminoazo-derivatives, for whereas with primary amines of the benzene series this reaction usually stops at an intermediate stage, giving rise to diazoamines,  $\text{R}\cdot\text{NH}_2\cdot\text{NHX}$ , yet compounds of this type have not been isolated in the case of *ar*-tetrahydro- $\alpha$ -naphthylamine, where the formation of an aminoazo-derivative seems to take place far more readily than with the similarly constituted *o*-2-xylidine (Noelting and Forel, *Ber.*, 1885, 18, 2682).

In view of this reactivity of *ar*-tetrahydro-*a*-naphthylamine towards diazo-compounds, it seemed desirable to ascertain whether the property of forming aminoazo-compounds directly was retained by its substitution products, and accordingly an attempt has been made to obtain certain of these derivatives and, after determining the orientation of the substituent radicles, to study the action of diazonium salts on the compounds in order to compare the results with those obtained in the benzene and naphthalene series.

Preliminary experiments on the nitration and chlorination of *ar*-tetrahydro-*a*-naphthylamine and its acyl derivatives showed that the changes involved were somewhat complex, whereas the ordinary processes of bromination and sulphonation led to the production of well-defined mono-substituted derivatives, and these were therefore examined in detail.

*Bromination of the Acyl Derivatives of ar-Tetrahydro-a-naphthylamine.*

Bamberger and Althausse (*Ber.*, 1888, 21, 1895) stated that on treating acetyl-*ar*-tetrahydro-*a*-naphthylamine with bromine in chloroform solution, the colour of the halogen immediately disappeared and a colourless acetylbromo-*ar*-tetrahydro-*a*-naphthylamine was produced. In our experiments, carried out under similar conditions, we found that the first substance to separate from the chloroform solution, after a considerable proportion of the bromine had been added, was an orange-yellow, crystalline compound, which had the properties of a perbromide and liberated iodine from potassium iodide. This product appears to result from the addition of bromine to the acetylbromo-*ar*-tetrahydro-*a*-naphthylamine, for it is also produced when bromine is added to a dry chloroform solution of the brominated acetyl derivative.

When the mixture is exposed for some time at the ordinary temperature, the yellow substance slowly disappears; this change is accelerated on warming, when the coloured substance dissolves in the chloroform, and the solution on cooling yields a colourless product, consisting chiefly of the acetylbromo-*ar*-tetrahydro-*a*-naphthylamine.

Similar results were obtained with the formyl, propionyl, and benzoyl derivatives of the tetrahydrogenated base (compare footnote, p. 745).

Acetyl-*ar*-tetrahydro-*a*-naphthylamine can also be brominated by means of hypobromous acid, the intermediate bromoamine thus produced being obtained as a pale yellow precipitate, which rapidly underwent isomeric change into acetylbromo-*ar*-tetrahydro-*a*-naphthylamine.

The brominated acetyl derivative prepared by either of the foregoing methods melted at 180—181°, and was therefore identical with the product obtained by Bamberger and Althausse (*loc. cit.*). When

hydrolysed, the acetyl derivative yielded the hydrochloride of a bromotetrahydro- $\alpha$ -naphthylamine melting at  $42^\circ$ .

The orientation of the substituent bromine atom was determined in the following manner. The base was diazotised in the ordinary way and the diazonium chloride solution treated with excess of alkaline sodium stannite; the product, when distilled in steam, yielded a volatile oil which had the properties of 1-bromotetrahydro-naphthalene, obtained by C. Smith from *ar*-tetrahydro- $\alpha$ -naphthylamine by means of the Sandmeyer reaction (compare this vol., p. 729).

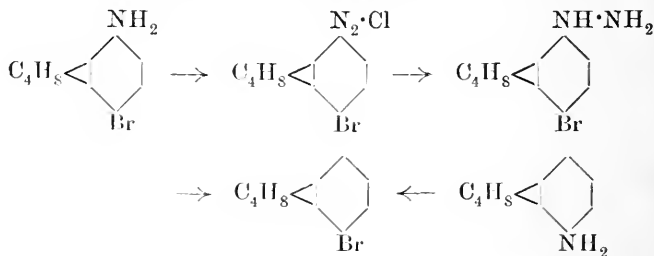
As the isomeric 2-bromotetrahydronaphthalene, prepared by the same investigator (*loc. cit.*) from *ar*-tetrahydro- $\beta$ -naphthylamine, is likewise an oil having a boiling point not far removed from that of the  $\alpha$ -compound, the two oily isomerides were nitrated with the view of obtaining, if possible, solid, crystalline nitro-derivatives.

2-Bromotetrahydronaphthalene, produced from the corresponding hydrogenated  $\beta$ -amine, when treated with a mixture of concentrated nitric and sulphuric acids, gave rise to a *dinitro*-derivative melting at  $105\text{--}106^\circ$ .

1-Bromotetrahydronaphthalene, obtained by replacing amidogen by bromine in *ar*-tetrahydro- $\alpha$ -naphthylamine by means of the Sandmeyer reaction, when similarly treated, readily yielded a *dinitro*-derivative melting at  $91^\circ$ .

Mixtures of the two dinitro-derivatives in approximately equal quantities melt at  $60\text{--}71^\circ$ , and therefore these compounds can be safely employed in identifying the two isomeric bromotetrahydronaphthalenes.

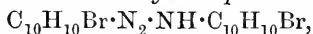
The bromo-compound, obtained by eliminating the amino-group from the new bromotetrahydro- $\alpha$ -naphthylamine, was accordingly nitrated, when it was found to give a dinitro-derivative, which melted at  $91^\circ$  and depressed considerably the melting point of the standard dinitro- $\beta$  compound (m. p.  $105\text{--}106^\circ$ ). The dinitro-compound was therefore derived from 1-bromotetrahydronaphthalene, and this result demonstrates that the bromine atom occupied the para-position with respect to the amino-group in the original bromo-base. Hence this compound is 4-bromotetrahydro- $\alpha$ -naphthylamine.



*The Action of Diazo-compounds on 4-Bromotetrahydro- $\alpha$ -naphthylamine and 4-Bromo- $\alpha$ -naphthylamine.*

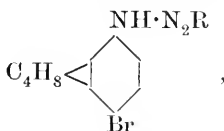
Since the bromo-base is a para-substituted compound, its reactions with diazonium salts should be compared with those of *p*-bromoaniline and 4-bromo- $\alpha$ -naphthylamine, its analogues in the benzene and naphthalene series respectively.

When two molecular proportions of 4-bromotetrahydro- $\alpha$ -naphthylamine are treated with one molecular proportion of nitrous acid, 4 : 4'-dibromo-1-diazo-1-aminotetrahydronaphthalene,



is produced. That this compound is really a diazoamine is shown by the fact that when treated with concentrated hydrochloric acid it is decomposed into a mixture of the hydrochlorides of its generators,  $\text{C}_{10}\text{H}_{10}\text{Br}\cdot\text{N}_2\cdot\text{Cl}$  and  $\text{C}_{10}\text{H}_{10}\text{Br}\cdot\text{NH}_2\cdot\text{HCl}$ . The diazonium base is detected by pouring the mixture into an alkaline solution of  $\beta$ -naphthol, when 4-bromotetrahydronaphthalene-1-azo- $\beta$ -naphthol (m. p.  $215^\circ$ ) is obtained; the regenerated amine is identified by conversion into its benzoyl derivative (m. p.  $202^\circ$ ).

4-Bromotetrahydro- $\alpha$ -naphthylamine behaves similarly towards other diazo-compounds, the product in every case being a diazoamine,



which undergoes the characteristic fission on treatment with concentrated mineral acids. The diazo-compounds employed were derived from the three nitroanilines, 6-aminocoumarin, and sulphanilic acid. In no case could the formation of an aminoazo-derivative be detected, and, moreover, it was not found possible to transform 4 : 4'-dibromo-1-diazo-1-aminotetrahydronaphthalene into its isomeric aminoazo-compound by digestion at  $70^\circ$  with a mixture of the bromo-base and its hydrochloride (compare Noetting and Witt, *Ber.*, 1884, 17, 78, and C. Smith, *Trans.*, 1902, 81, 900).

As regards its behaviour towards diazo-compounds, 4-bromotetrahydro- $\alpha$ -naphthylamine therefore resembles *p*-bromoaniline, which also gives rise to stable diazoamines.

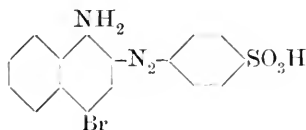
The action of nitrous acid (1 mol.) on 4-bromo- $\alpha$ -naphthylamine (2 mols.) leads to the formation of a somewhat ill-defined product which consists chiefly of an azo-compound, but although the experimental conditions were varied, it was not possible to obtain the sub-

stance in a state of purity, yet its colour, stability towards hot hydrochloric acid, and the development of an intense blue coloration with cold concentrated sulphuric acid suggest that it is an aminoazo-compound having the formula  $C_{10}H_6BrN_2 \cdot C_{10}H_5Br \cdot NH_2$ .

This view was confirmed by the preparation of more definite products by the action of other diazonium salts on the bromo-base. The compounds produced from the diazotised nitroanilines were isolated in a state of purity and were found to be dark reddish-brown substances not decomposed by hot concentrated hydrochloric acid in aqueous or alcoholic solutions; moreover, they developed characteristic colorations with cold concentrated sulphuric acid and yielded acetyl and benzoyl derivatives by the ordinary processes.

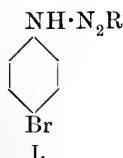
A final confirmation of the hypothesis that these compounds are azo-derivatives was furnished by the reduction of the compound  $SO_3H \cdot C_6H_4N_2 \cdot C_{10}H_5Br \cdot NH_2$ , obtained from the bromo-base and diazobenzenesulphonic acid.

This azo-colouring matter, when treated with tin and hot alcoholic hydrochloric acid, was reduced to sulphanilic acid and naphthylene-1:2-diamine (m. p. 95—96°), the destruction of the azo-linking and the elimination of bromine from the naphthalene nucleus taking place simultaneously. The latter compound was identified as an ortho-diamine by the production of its azine,  $C_{10}H_6 \begin{smallmatrix} N \\ < \\ N \end{smallmatrix} C_{14}H_8$  (m. p. 273°), with phenanthraquinone (Lawson, *Ber.*, 1885, 18, 2426), and also characterised by the formation of its diacetyl derivative (m. p. 234°). The original azo-colouring matter has therefore the constitution expressed by the following formula:

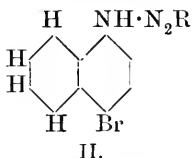


In short, the interaction of diazo-compounds and 4-bromo- $\alpha$ -naphthylamine always leads to the direct formation of azo-derivatives, the constitution of which may be indicated by the general formula III. As *p*-bromoaniline is known to give stable diazoamines which have not been hitherto transformed into the isomeric aminoazo-derivatives, it follows that 4-bromotetrahydro- $\alpha$ -naphthylamine in its behaviour towards diazo-compounds resembles the analogously constituted benzenoid bases and differs entirely from 4-bromo- $\alpha$ -naphthylamine.

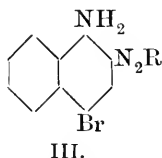
The products obtained in the three series under comparison may be therefore symbolised in the following manner:



Benzene series.



Tetrahydronaphthalene series.



Naphthalene series.

These results therefore justify Bamberger's general conclusions as to the assumption of a benzenoid character by the tetrahydronaphthylamines, owing to the hydrogenation of the unsubstituted ring (compare C. Smith, *loc. cit.*).

### *Sulphonation of ar-Tetrahydro- $\alpha$ -naphthylamine.*

The sulphonation of *ar*-tetrahydro- $\alpha$ -naphthylamine with ordinary concentrated sulphuric acid at moderate temperatures leads to the production of a monosulphonic acid, the constitution of which was established in the following manner.

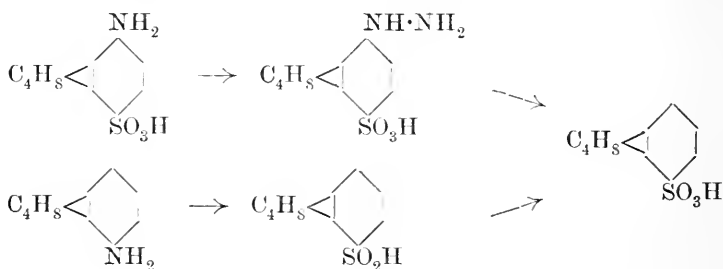
The aminosulphonic acid was successively converted into the diazo-derivative,  $C_{10}H_{10} \begin{smallmatrix} \text{N}_2 \\ \diagup \text{SO}_3 \end{smallmatrix}$ , and the hydrazine,  $NH_2 \cdot NH \cdot C_{10}H_{10} \cdot SO_3H$ , the latter being then boiled with copper sulphate solution (Baeyer and Pfizinger, *Ber.*, 1885, 18, 90, 786) in order to eliminate the hydrazino-radicle. The tetrahydronaphthalenesulphonic acid thus produced was isolated in the form of its barium salt, and from this substance the corresponding sulphonic chloride (m. p.  $70.5^\circ$ ) and sulphonanilide (m. p.  $144-145^\circ$ ) were successively prepared.

Two *ar*-tetrahydronaphthalenesulphonic acids are theoretically possible containing the sulphonic group in either the  $\alpha(=1)$ - or the  $\beta(=2)$ -position.

A sulphonic acid obtained by the direct sulphonation of tetrahydronaphthalene has been described by Graebe and Guye (*Ber.*, 1883, 16, 3031) and another by Bamberger and Kitschelt (*Ber.*, 1890, 23, 1563), but it is not possible to state with certainty from the existing data whether either of these substances is identical with the compound obtained in the foregoing experiments.

Since in the preceding bromination the entrant radicle took up the para-position with respect to the acylamino-group, it seemed likely that the sulphonic group would displace the same hydrogen atom of the aromatic nucleus, in which case the synthesised tetrahydronaphthalenesulphonic acid should be the  $\alpha$ -compound. *ar*-Tetrahydro- $\alpha$ -naphthylamine sulphate was diazotised and converted into *tetrahydronaphthalene-1-sulphinic acid* by the action of sulphurous acid and copper powder (Gatterman, *Ber.*, 1899, 32, 1136). The sulphinic

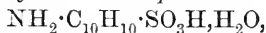
acid was oxidised with potassium permanganate to *tetrahydronaphthalene-1-sulphonic acid*, the potassium salt of which was converted successively into *tetrahydronaphthalene-1-sulphonic chloride* and *tetrahydronaphthalene-1-sulphonanilide*; these derivatives melted respectively at  $70.5^\circ$  and  $144\text{--}145^\circ$ , and were found to be identical with the chloride and anilide derived from the sulphonic acid obtained synthetically from *ar*-tetrahydro- $\alpha$ -naphthylaminesulphonic acid. Hence this amino-acid must contain its sulphonic group in the para-position with respect to the amino-radicle. The chemical changes involved in this demonstration may be thus indicated:



The fact that tetrahydronaphthalene-1-sulphonic acid may be produced by two distinct series of operations, including reactions of a somewhat dissimilar nature, tends to show that the hydrogenated residue  $\text{C}_4\text{H}_8$  does not undergo any change during the sulphonation of the *ar*-tetrahydro- $\alpha$ -naphthylamine, and confirmatory evidence was obtained by the direct comparison of tetrahydronaphthalene-1-sulphonic chloride (m. p.  $70.5^\circ$ ) with naphthalene-1-sulphonic chloride (m. p.  $66^\circ$ ), when a mixture of the two compounds was found to melt at  $45\text{--}47^\circ$ .

The sulphonic chloride and the bromodinitrotetrahydronaphthalenes obtained in the experiments recorded on p. 738 were tested with bromine in chloroform solution and were found not to decolorise this reagent, thus behaving as saturated compounds; this negative result excludes the possibility of the substances being derivatives of dihydronaphthalene and furnishes additional evidence in favour of the view that the hydrogenated ring has not undergone any change.

*ar*-Tetrahydro- $\alpha$ -naphthylamine-4-sulphonic acid,



when treated with a diazo-compound such as *p*-nitrobenzenediazonium chloride, yields a diazoamine which undergoes the characteristic fission with concentrated hydrochloric acid. In this respect, therefore, the hydrogenated amino-acid differs essentially from naphthionic acid ( $\alpha$ -naphthylamine-4-sulphonic acid), which, under these conditions, is known to give azo-colouring matters.

The foregoing study of the products of the interaction of diazo-

compounds and 4-bromotetrahydro- $\alpha$ -naphthylamine and *ar*-tetrahydro- $\alpha$ -naphthylamine-4-sulphonic acid shows that as regards this condensation the para-substituted *ar*-tetrahydro- $\alpha$ -naphthylamine derivatives differ entirely from the similarly constituted naphthalene compounds and leads to the conclusion that the reactivity of the hydrogen atom in the ortho-position adjacent to the amino-group is a characteristic feature of the naphthalene molecule which is destroyed when the non-substituted ring undergoes hydrogenation.

The azo-compounds of *ar*-tetrahydro- $\alpha$ -naphthylamine were first described by Bamberger and Bordt (*Ber.*, 1889, 22, 625), and other members of this series have been since prepared by C. Smith (*loc. cit.*). These substances, like the corresponding azo-derivatives of  $\alpha$ -naphthylamine, can be readily diazotised and the resulting diazo-compounds recombined with the sulphonic acids of the phenols or aromatic amines to yield disazo-colouring matters.

The azo-compound from diazobenzenesulphonic acid and *ar*-tetrahydro- $\alpha$ -naphthylamine, when dyed on wool in an acid bath, produces a bright orange colour, whereas the corresponding azo-derivative from  $\alpha$ -naphthylamine furnishes a dull brown shade. In order to ascertain whether these compounds, which differ so markedly in tinctorial properties, are both para-azo-derivatives, they were reduced with tin and hydrochloric acid under comparable conditions. The results obtained with  $\alpha$ -naphthylamineazobenzene-4-sulphonic acid confirm those already described by Griess (*Ber.*, 1882, 15, 2192), for the reduction products were sulphanilic acid and naphthylene-1 : 4-diamine (m. p. 120°), the latter being also characterised by the formation of its diacetyl derivative (m. p. 305°) and by its oxidation to  $\alpha$ -naphthaquinone.

The azo-acid from *ar*-tetrahydro- $\alpha$ -naphthylamine yielded on reduction sulphanilic acid and *ar*-tetrahydronaphthylene-1 : 4-diamine, the latter being identified as a para-diamine by yielding tetrahydronaphthaquinone on oxidation (Bamberger and Lengfeld, *Ber.*, 1890, 23, 1132). The azo-derivative is therefore *ar*-tetrahydro- $\alpha$ -naphthylamine-4-azobenzene-4'-sulphonic acid, and the striking contrast between its tinctorial properties and those of  $\alpha$ -naphthylamine-4-azobenzene-4'-sulphonic acid is due, not to any difference in the orientation of the azo-group with respect to the amino-radicle, but must be regarded as being the result of the profound change produced in the aromatic nucleus by the hydrogenation of the unsubstituted ring.

## EXPERIMENTAL.

*The Action of Bromine on the Acyl Derivatives of  $\alpha$ -Tetrahydro- $\alpha$ -naphthylamine.*

The tetrahydro- $\alpha$ -naphthylamine required in the following experiments was obtained by reducing batches of 45 grams of  $\alpha$ -naphthylamine, dissolved in 600 c.c. of boiling amyl alcohol, with 40 grams of sodium, the metal being added in large lumps so as to render the action as vigorous as possible. After purifying the product in the manner indicated by Bamberger and Althausse (*loc. cit.*), 321 grams of rectified tetrahydro-base, boiling at 275—277° (uncorr.), were obtained from 450 grams of crude  $\alpha$ -naphthylamine.

Acetyltetrahydro- $\alpha$ -naphthylamine was prepared by heating the tetrahydro-base for about 2—4 hours with an equal weight of glacial acetic acid containing about 8 per cent. of acetic anhydride, the crude acetyl derivative being crystallised from benzene; it then melted at 154°.

On adding 2.5 grams of bromine (1 mol.) dissolved in 15 c.c. of chloroform to a solution of 3 grams of the acetyl derivative in 25 c.c. of the same solvent, an orange-coloured, crystalline precipitate slowly separated, and the action was accompanied by a comparatively slight evolution of hydrogen bromide. This precipitate, which retained its yellow colour even after repeated washing with chloroform, was collected and found to weigh 3 grams. The filtrate was carefully evaporated to a small bulk, when a further quantity of the yellow substance was obtained, weighing 2.2 grams. The final filtrate, when evaporated to dryness, deposited a very small amount of oily matter.

The yellow compound was analysed for perbromide bromine by agitating with a mixture of chloroform and aqueous potassium iodide, and then titrating with standard thiosulphate solution. The first and second crops contained 21.0 and 20.0 per cent. of active bromine respectively. The amount of active bromine varied within 2 or 3 per cent. in different experiments, but the results seemed to indicate that approximately half the bromine combined additively with the acetyl derivative, yielding a perbromide which is fairly stable in a dry atmosphere at the ordinary temperature.

In the foregoing experiments, the materials were moderately dry, the chloroform having been distilled from calcium chloride containing a small amount of quicklime, and then kept over phosphoric oxide; the bromine had also been dried with this dehydrating agent; the recrystallised acetyl derivative was heated for 2 hours at 100° and allowed to cool in a desiccator. The reagents were mixed at the ordinary temperature. When the mixture in chloroform was

kept for several days, the precipitate gradually became colourless, and on warming on the water-bath the product was completely decolorised. The precipitate was then collected, when it was found that 14 grams were obtained from 10 grams of the original acetyl compound, only a small quantity of impure substance remaining in the filtrate. The colourless compound, when crystallised from either ethyl acetate or benzene, separated in felted needles melting at  $180-181^{\circ}$ ; it was apparently identical with the acetylbromotetrahydro- $\alpha$ -naphthylamine obtained by Bamberger and Althausse (*loc. cit.*).

The bromination was repeated with undried materials, employing glacial acetic acid as solvent, but in this case also the orange-yellow substance was first produced, and only slowly changed into the colourless compound, a few crystals of the latter being seen after three days. On heating the mixture containing the intermediate product, the latter dissolved, evolving hydrogen bromide, and the solution when cooled, yielded the colourless acetyl derivative.\*

#### *4-Bromotetrahydro- $\alpha$ -naphthylamine.*

*4-Bromotetrahydro- $\alpha$ -naphthylamine* was obtained by boiling the foregoing acetyl compound (14 grams) with 20 c.c. of concentrated hydrochloric acid and 20 c.c. of alcohol in a reflux apparatus for 2—3 hours. The hydrochloride of the base crystallised out on cooling in glistening, colourless plates, and was decomposed by ammonia, the crude base being dried and crystallised repeatedly from a mixture of equal volumes of benzene and light petroleum, when it separated in slender, colourless needles melting at  $42^{\circ}$ .

0.1895 gave 0.1574 AgBr. Br = 35.35.

0.2392 „ 13 c.c. moist nitrogen at  $18^{\circ}$  and 762 mm. N = 6.29.

$C_{10}H_{12}NBr$  requires Br = 35.40. N = 6.19 per cent.

The base is very soluble in the ordinary organic solvents excepting light petroleum; it is slightly volatile in steam.

*Formyl-4-bromotetrahydro- $\alpha$ -naphthylamine*,  $C_{10}H_{10}Br \cdot NH \cdot CHO$ , obtained by heating equal parts of the base and formic acid (sp. gr. 1.2) for half an hour, crystallised from benzene or alcohol in colourless plates melting at  $164.5^{\circ}$ .

\* It has been found that acetylbromotetrahydro- $\alpha$ -naphthylamine, and also the corresponding formyl, propionyl, and benzoyl derivatives, yield crystalline, orange-yellow perbromides when treated with bromine in chloroform solution. Moreover, acetyl-*p*-bromoaniline, under comparable conditions, gives rise to a similar additive compound. A study of these intermediate products of the action of bromine on the acyl derivatives of aromatic amines will form the subject of a separate investigation.

0.1828 gave 9.3 c.c. moist nitrogen at 18° and 752 mm.  $N = 5.81$ .  
 $C_{11}H_{12}ONBr$  requires  $N = 5.51$  per cent.

The formyl derivative, when treated with bromine in chloroform, yields a yellow additive product, which changes into a colourless substance giving an oily base on hydrolysis with alcoholic hydrochloric acid and subsequent treatment with ammonia. This oil, on treatment with acetic anhydride, yields an acetyl derivative melting at 198—199° and containing 45.65 per cent. of bromine, the calculated amount for an acetylated dibromo-base being 46.11. This compound will be further investigated.

*Propionyl-4-bromotetrahydro- $\alpha$ -naphthylamine,*



was produced on mixing together 10 grams of the bromo-base 5 grams of propionic acid, and 2 c.c. of propionic anhydride, the solid which appeared immediately being crystallised from chloroform; it separated in colourless needles melting at 185—186°.

0.1173 gave 0.0767 AgBr.  $Br = 27.83$ .

0.1554 „ 7.3 c.c. moist nitrogen at 18° and 747 mm.  $N = 5.33$ .

$C_{13}H_{16}ONBr$  requires  $Br = 28.39$ ;  $N = 4.96$  per cent.

*Benzoyl-4-bromotetrahydro- $\alpha$ -naphthylamine,*  $C_{10}H_{10}Br \cdot NH \cdot CO \cdot C_6H_5$ , prepared by the Schotten-Baumann process, crystallised from alcohol in colourless needles melting at 202—203°.

0.1199 gave 0.0668 AgBr.  $Br = 23.77$ .

$C_{17}H_{16}ONBr$  requires  $Br = 24.24$  per cent.

*Conversion of 4-Bromotetrahydro- $\alpha$ -naphthylamine into 1-Bromotetrahydronaphthalene.*

A mixture of 6.3 grams of recrystallised 4-bromotetrahydro- $\alpha$ -naphthylamine, suspended in 13 grams of concentrated hydrochloric acid diluted with 25 c.c. of water, was thoroughly cooled and treated with 2 grams of sodium nitrite in 10 per cent. aqueous solution. The diazotisation took place moderately readily, and after stirring the mixture vigorously in a mortar, the whole changed into a pale yellow solution, which was added to a cooled 30 per cent. caustic soda solution. The crimson solution thus produced was then slowly added to a solution prepared by dissolving 20 grams of crystallised stannous chloride in 30 per cent. aqueous caustic soda. At 0°, an orange-coloured solid was deposited; the mixture was left for one hour at the ordinary temperature, then warmed, and distilled in steam. About 2 c.c. of oil were obtained in the distillate accompanied by a red, tarry substance. The mixture was extracted with ether, the extract dried over calcium

chloride, the solvent then evaporated off, and the residue distilled. The residual oil boiled at 260—265° and appeared to be identical with the 1-bromotetrahydronaphthalene obtained by C. Smith on subjecting *ar*-tetrahydro- $\alpha$ -naphthylamine to the Sandmeyer reaction in the presence of hydrobromic acid and cuprous bromide; a specimen of the oily bromo-compound thus prepared also boiled at 260—265°.

The identity of the two products was further established in the following manner by the production of a definitely crystalline dinitro-compound.

*1-Bromodinitrotetrahydronaphthalene*.—Five parts of 1-bromotetrahydronaphthalene, obtained from tetrahydro- $\alpha$ -naphthylamine were suspended in 30 parts of cold concentrated sulphuric acid and treated with 3.5 parts of concentrated nitric acid (sp. gr. 1.4) mixed with 7 parts of concentrated sulphuric acid. A pale yellow substance was precipitated, the mixture was then poured on to ice, the precipitate collected, washed, and crystallised from light petroleum, when it separated in pale yellow, transparent plates or nodules; after two or three crystallisations from this solvent, the compound melted at 91°.

0.0992 gave 0.0622 AgBr. Br = 26.68.

0.2355 „ 20.1 c.c. moist nitrogen at 19° and 748 mm. N = 9.64.

$C_{10}H_9O_4N_2Br$  requires Br = 26.57; N = 9.30 per cent.

On repeating this nitration with the 1-bromotetrahydronaphthalene obtained from 4-bromotetrahydro- $\alpha$ -naphthylamine, a solid bromodinitrotetrahydronaphthalene was produced which melted at 91° and did not depress the melting point of the foregoing preparation.

As the proof of the constitution of 4-bromotetrahydro- $\alpha$ -naphthylamine depends on the foregoing results, it seemed desirable to ascertain the nature of the product obtained by nitrating the isomeric 2-bromotetrahydronaphthalene first obtained by C. Smith (this vol., p. 729).

*2-Bromodinitrotetrahydronaphthalene*.—2-Bromotetrahydronaphthalene, prepared from *ar*-tetrahydro- $\beta$ -naphthylamine by the Sandmeyer reaction in the presence of hydrobromic acid and cuprous bromide, was treated with a mixture of nitric and sulphuric acids as in the preceding experiment. The nitration appeared to take place less readily in this instance, the crude product being somewhat viscid. When repeatedly extracted with light petroleum (b. p. 40—60°), an uncrystallisable resin remained undissolved, whilst the solution deposited rosettes of well-defined, pale yellow needles which, when recrystallised from the same solvent, melted at 105—106°, softening slightly at 103°.

0.2387 gave 0.1517 AgBr. Br = 27.04.

0.0992 „ 8.3 c.c. moist nitrogen at 16° and 761 mm. N = 9.76.

$C_{10}H_9O_4N_2Br$  requires Br = 26.57; N = 9.30 per cent.

Mixtures of approximately equal parts of this dinitro-compound with its  $\alpha$ -isomeride melt at temperatures varying from 61—72°.

*Comparative Experiments on the Behaviour of 4-Bromotetrahydro- $\alpha$ -naphthylamine and 4-Bromo- $\alpha$ -naphthylamine towards Diazo-compounds.*

*Diazoamines derived from 4-Bromotetrahydro- $\alpha$ -naphthylamine.*

4:4'-Dibromo-1-diazo-1-aminotetrahydronaphthalene was obtained on condensing the hydrogenated base with its own diazonium chloride. Twelve grams of the powdered base were suspended in 19 c.c. of concentrated hydrochloric acid diluted with an equal volume of ice-cold water and treated with 3.6 grams of sodium nitrite in 10 per cent. solution. A solution of 12 grams of the base in glacial acetic acid was then added to the clear solution of the diazonium salt and the mixture treated with 18 grams of crystallised sodium acetate. The yellow diazoamine (20 grams) separated immediately and was subsequently crystallised from benzene; it separates from this solvent in orange-yellow needles and decomposes violently at 190—194°.

0.3872 gave 30.6 c.c. moist nitrogen at 17° and 757 mm.  $N = 9.14$ .

0.1949 „ 0.1562 AgBr.  $Br = 34.10$ .

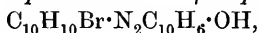
$C_{20}H_{21}N_3Br_2$  requires  $N = 9.07$ ;  $Br = 34.50$  per cent.

The substance is almost insoluble in alcohol, acetone, or ethyl acetate. When treated with cold concentrated hydrochloric acid, the diazoamine slowly undergoes fission into its generators, but owing to its sparing solubility the decomposition occurs very slowly. About 0.6 gram of the substance was treated with an alcoholic solution containing 9 grams of hydrogen chloride; the solution was then diluted with water and filtered into an alkaline solution of  $\beta$ -naphthol, the insoluble azo-compound produced, when washed with acid and alkali and weighed, was found to represent 90 per cent. of the hydrolysed diazoamine, about 0.15 gram of the unchanged diazoamine being recovered.

The diazoamine does not develop a coloration with cold concentrated sulphuric acid, this result indicating the absence of any appreciable amount of the isomeric azo-compound in the substance; it is almost insoluble in this medium, and providing that the latter is kept in a dry atmosphere no fission takes place. On diluting the acid by pouring the mixture on to ice, the diazoamine is rapidly hydrolysed, yielding the soluble 4-bromotetrahydro- $\alpha$ -naphthalenediazonium sulphate and the sparingly soluble 4-bromotetrahydro- $\alpha$ -naphthylamine sulphate; the former was characterised by filtering the solution into an alkaline solution of  $\beta$ -naphthol, whilst the latter was identified by sub-

jecting the precipitate to the Schotten-Baumann reaction, when benzoyl-4-bromotetrahydro- $\alpha$ -naphthylamine was produced which melted at 202°.

4-Bromotetrahydro-1-naphthalene-1'-azo- $\beta$ -naphthol,



was also prepared from diazotised 4-bromotetrahydro- $\alpha$ -naphthylamine and  $\beta$ -naphthol in the ordinary way; it is sparingly soluble in alcohol, ethyl acetate, or acetone, and dissolves more readily in glacial acetic acid or pyridine, crystallising in red needles with a bronzy reflex.

0.1268 gave 8.4 c.c. moist nitrogen at 17° and 758 mm. N = 7.45.

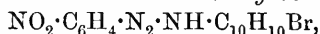
0.3270 „ 0.1590 AgBr. Br = 20.70.

$\text{C}_{20}\text{H}_{17}\text{ON}_2\text{Br}$  requires N = 7.34; Br = 20.99 per cent.

This preparation, as well as those obtained from the fission products of the diazoamine, melted at 215°.

An attempt was made to transform the diazoamine into an isomeric aminoazo-compound by warming it at 70° with a mixture of 4-bromotetrahydro- $\alpha$ -naphthylamine and its hydrochloride, either alone or with pyridine as a solvent. Under these conditions, an azo-derivative could not be detected among the tarry products thus obtained.

*p*-Nitrobenzenediazo-1-amino-4-bromotetrahydronaphthalene,



was obtained by mixing a solution of *p*-nitrobenzenediazonium chloride (1 mol.), prepared in the ordinary way, with a glacial acetic acid solution of 4-bromotetrahydro- $\alpha$ -naphthylamine (1 mol.) and treating the mixture with excess of sodium acetate. The precipitated diazoamine was washed with water, dried, and crystallised from benzene; it separated in brownish-yellow leaflets and decomposed violently at about 178°.

0.1862 gave 24.3 c.c. moist nitrogen at 15° and 743 mm. N = 14.93.

0.3790 „ 0.1872 AgBr. Br = 21.02.

$\text{C}_{16}\text{H}_{15}\text{O}_2\text{N}_4\text{Br}$  requires N = 14.93; Br = 21.33 per cent.

*o*-Nitrobenzenediazo-1-amino-4-bromotetrahydronaphthalene, produced in exactly the same manner as the preceding compound, crystallised from benzene in orange-brown needles and decomposed violently at 170—175°.

0.0986 gave 13 c.c. moist nitrogen at 15° and 743 mm. N = 15.08.

0.1801 „ 0.0876 AgBr. Br = 20.70 per cent.

The isomeric *diazoamine* prepared from *m*-nitroaniline crystallised from benzene in orange-brown prisms and decomposed violently at 165—166°.

0.1666 gave 22.2 c.c. moist nitrogen at 17° and 742 mm. N = 15.09.  
 0.2052 „ 0.1016 AgBr. Br = 21.08 per cent.

The foregoing diazoamines from *o*- and *p*-nitroanilines dissolve in alcoholic alkali hydroxides to an intense bluish-crimson solution, whilst the *m*-isomeride develops a brownish-red coloration.

Diazobenzenesulphonic acid also yields with 4-bromotetrahydro-*a*-naphthylamine a pale yellow diazoamine which gives a crimson coloration in alcoholic potash.

*Coumarin-6-diazo-1-amino-4-bromotetrahydronaphthalene,*



was prepared in order to compare the action of diazotised 6-amino-coumarin on the tetrahydrogenated bromo-base with that of the same diazo-compound on 4-bromo-*a*-naphthylamine (see p. 751); on adding an excess of sodium acetate to an alcoholic solution of its generators, it is obtained as a pale yellow precipitate which is sparingly soluble in benzene and the other organic solvents. It separates in ill-defined, brownish-yellow, nodular crystals and decomposes at 165—168°.

0.1898 gave 16.5 c.c. moist nitrogen at 14° and 762 mm. N = 10.26.

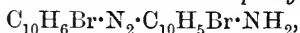
$\text{C}_{19}\text{H}_{16}\text{O}_2\text{N}_3\text{Br}$  requires N = 10.55 per cent.

When warmed with concentrated hydrochloric acid, the foregoing diazoamines are all decomposed, evolving nitrogen.

#### *Azo-derivatives of 4-Bromo- $\alpha$ -Naphthylamine.*

The 4-bromo-*a*-naphthylamine required in the following experiments was prepared by brominating aceto-*a*-naphthalide with 1 molecular proportion of bromine in glacial acetic acid solution, crystallising the acetyl bromo-compound from the same solvent, and hydrolysing it by boiling with excess of 50 per cent. caustic potash solution in an open vessel until the product became quite oily. The base was then collected and crystallised from benzene and petroleum until it melted at 94—95°.

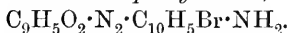
*4'-Bromo-1-naphthalene-2-azo-4-bromo- $\alpha$ -naphthylamine,*



was obtained most conveniently by diazotising 4-bromo-*a*-naphthylamine (2 grams), suspended in a mixture of 3.5 c.c. of concentrated hydrochloric acid and 75 c.c. of glacial acetic acid, the nitrite being in a 20 per cent. solution. To the clear brown solution thus obtained were added successively 2 grams of the original base dissolved in glacial acetic acid and 10 grams of hydrated sodium acetate, when the red azo-compound separated immediately. This substance does not crystallise readily from glacial acetic acid, ethyl acetate, or pyridine,

and is very sparingly soluble in alcohol; it was dissolved in benzene, and the solution, on spontaneous evaporation, deposited the azo-compound as a red powder which darkens at  $178^{\circ}$  and melts at  $181-182^{\circ}$ . Although the substance was not obtained quite pure, the analysis showed that it was an azo-derivative having the above formula. The percentages of nitrogen and bromine in the compound were found to be 10.51 and 33.81 respectively, whereas  $C_{20}H_{13}N_3Br_2$  requires  $N=9.45$  and  $Br=35.16$  per cent. The condensation was repeated in aqueous and pyridine solutions, but the results were even less favourable than the foregoing. This azo-compound develops an intense greenish-blue coloration with cold concentrated sulphuric acid.

*Coumarin-6'*: 2-azo-4-bromo-*a*-naphthylamine,



—6-Aminocoumarin (1 mol.) was diazotised in the ordinary way and the light brown solution of the diazonium chloride added to an alcoholic solution of 4-bromo-*a*-naphthylamine (1 mol.); a dark red precipitate was at once produced, and this became bright scarlet on adding excess of sodium acetate. The azo-compound is very insoluble in the ordinary solvents; it separates from glacial acetic acid in brownish-red nodules melting at  $240-241^{\circ}$ .

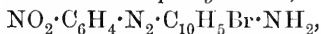
0.2574 gave 23.2 c.c. moist nitrogen at  $18^{\circ}$  and 762 mm.  $N=10.45$ .

0.1012 „ 0.486 AgBr.  $Br=20.44$ .

$C_{19}H_{12}O_2N_3Br$  requires  $N=10.65$ ;  $Br=20.30$  per cent.

With cold concentrated sulphuric acid, the azo-compound develops a brownish-red coloration.

*p*-Nitrobenzene-2-azo-4-bromo-*a*-naphthylamine,



when prepared by adding a dilute hydrochloric acid solution of *p*-nitrobenzenediazonium chloride (1 mol.) to a 2 per cent. alcoholic solution of the bromo-base, separates as a dark brownish-red precipitate which does not crystallise readily from the ordinary solvents. After one crystallisation from alcohol, it melted indefinitely at  $194-200^{\circ}$ , and when repeatedly crystallised from the same solvent it separated in dark reddish-brown crystals and melted sharply at  $201-202^{\circ}$ . In all probability this melting point is still too low, for both the isomerides of this azo-compound melt at higher temperatures, whereas the para-compound is usually the least fusible.

0.1470 gave 18.8 c.c. moist nitrogen at  $18^{\circ}$  and 754 mm.  $N=14.66$ .

0.1509 „ 0.0750 AgBr.  $Br=21.16$ .

$C_{16}H_{11}O_2N_4Br$  requires  $N=15.09$ ;  $Br=21.56$  per cent.

This compound develops a reddish-purple coloration with cold concentrated sulphuric acid.

*o*-Nitrobenzene-2-azo-4-bromo-*a*-naphthylamine, produced exactly like the foregoing compound, was crystallised successively from glacial acetic acid and benzene and was then obtained in well-defined, dark brown needles with a dark bronzy reflex; it melted at 219—220° and developed an intense purple coloration with cold concentrated sulphuric acid.

0.1309 gave 16.9 c.c. moist nitrogen at 13° and 762 mm.  $N = 15.30$ .

0.1902 „ 0.0952 AgBr.  $Br = 21.30$

$C_{16}H_{11}O_2N_4Br$  requires  $N = 15.09$ ;  $Br = 21.56$  per cent.

*m*-Nitrobenzene-2-azo-4-bromo-*a*-naphthylamine, was produced by diazotising *m*-nitroaniline in 15 per cent. aqueous hydrochloric acid and adding the diazo-solution to an alcoholic solution of the bromo-base (1 mol.), when the azo-compound separated at once as an amorphous, red precipitate. This product, when crystallised from pyridine, separated in minute, reddish-brown leaflets which were boiled repeatedly with alcohol to remove all traces of the basic solvent. The substance then melted at 246° and gave a brownish-red coloration with concentrated sulphuric acid.

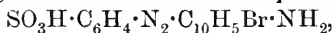
0.2207 gave 28.6 c.c. moist nitrogen at 14° and 760 mm.  $N = 15.26$ .

0.4246 „ 0.2100 AgBr.  $Br = 21.06$ .

$C_{16}H_{11}O_2N_4Br$  requires  $N = 15.26$ ;  $Br = 21.56$  per cent.

The foregoing aminoazo-compounds are not decomposed on boiling for 1—2 hours with alcohol saturated with hydrogen chloride. The hydrochloride of the aminoazo-base is produced, and this, when separated and treated with ammonia, regenerates the original compound. The azo-derivative from *p*-nitroaniline, when subjected to this cycle of operations, still melted at 201—202°.

4-Bromo-*a*-naphthylamine-2-azobenzene-4'-sulphonic acid,



which was produced on adding diazobenzene-*p*-sulphonic acid suspended in water to an alcoholic solution of the bromo-base, separated immediately as a reddish-black precipitate, which on drying exhibits a bronzy-green reflex. A portion was converted into the sodium salt by warming with aqueous sodium carbonate, and the free acid, reprecipitated from the boiling solution, was thoroughly washed with water and dried, when it had a dark green colour. Although this substance was not further purified, an analysis of the precipitated colouring matter when dried in air, showed that it still contained bromine, and was therefore not formed by a replacement of this halogen by the diazo-group.

0.2371 gave 0.1229 AgBr.  $Br = 17.52$ .

$C_{16}H_{12}O_3N_3BrS$  requires  $Br = 19.7$  per cent.

This azo-sulphonic acid develops a red coloration with concentrated sulphuric acid, and when dyed on wool in an acid bath it furnishes a reddish-brown colour.

*Reduction of 4-Bromo- $\alpha$ -naphthylamine-2-azobenzene-4'-sulphonic Acid.*

The foregoing azo-colouring matter was dissolved in the calculated amount of sodium carbonate and the hot saturated solution of the sodium salt added gradually to a mixture of granulated tin and boiling alcoholic hydrochloric acid (1 vol. alcohol : 1 vol. concentrated acid); the azo-acid was set free and rapidly reduced, the clear brown solution being then concentrated to a small bulk and cooled. A crystalline product separated which was shaken up with excess of aqueous caustic potash and extracted with ether, the ethereal extract being decanted and filtered from the precipitated tin compounds. The ether was then removed on the water-bath, and the residual oil cooled in ice until brown crystals separated; these were extracted repeatedly with light petroleum (b. p. 40—80°). The petroleum extracts on cooling deposited light brown, nodular crystals, which did not contain bromine and melted at 94°. This substance was identified as naphthylene-1:2-diamine by the melting point, which was given by Lawson (*Ber.*, 1885, 18, 800) as 95—96°. Further confirmation was afforded by the formation of the diacetyl derivative, and the azine with phenanthraquinone. In preparing the diacetyl derivative, an excess of acetic anhydride was added to a portion of the ethereal extract from the products of reduction; the product rapidly separated in brownish-white crystals, and was recrystallised from alcohol, when it formed well-defined, colourless needles melting at 233—234°; Lawson (*loc. cit.*) gives the melting point as 234°.

The brown, nodular crystals of the diamine obtained on cooling the oily residue from the ethereal extract were mixed with a slight excess of hydrochloric acid, the dihydrochloride was partially dissolved in alcohol and boiled for 20 minutes with a glacial acetic acid solution of phenanthraquinone, the azine, which separated almost immediately as a brown, micro-crystalline deposit, was crystallised from benzene, and separated from this solvent in small, golden-yellow spangles with a brown reflex; it melted at 272—273°, this temperature being identical with the melting point given by Lawson (*Ber.*, 1885, 18, 2426). This azine dissolves in cold concentrated sulphuric acid to an intense peacock-blue solution, the colour of which is destroyed on dilution with water.

*Reduction of ar-Tetrahydro- $\alpha$ -naphthylamine-4-azobenzene-4'-sulphonic Acid.*

*ar*-Tetrahydro- $\alpha$ -naphthylamine-4-azobenzene-4'-sulphonic acid was prepared by adding an alcoholic solution of *ar*-tetrahydro- $\alpha$ -naphthylamine to diazobenzene-*p*-sulphonic acid suspended in cold water, when it separated in lustrous, yellow leaflets, which were converted into the sodium salt by the addition of sodium carbonate. The mixture was heated until the soluble sodium salt was dissolved, and then allowed to cool, when the salt crystallised in yellowish-brown leaflets. When dyed on wool in an acid bath, this azo-compound furnishes a bright orange colour quite unlike the chocolate shade produced by its analogue,  $\alpha$ -naphthylamine-4-azobenzene-4'-sulphonic acid.

A saturated solution of the sodium salt of the tetrahydronaphthalene derivative was slowly added to a mixture of tin and hot alcoholic hydrochloric acid and the reduction carried out precisely as in the preceding experiment. The crystalline product, obtained on concentrating and cooling the colourless solution, when rendered alkaline with strong aqueous caustic potash and extracted with ether, yielded a highly oxidisable base, which separated from the ethereal solution in colourless needles, rapidly turning green on exposure. The ethereal solution was accordingly treated with excess of acetic anhydride and the precipitated acetyl derivative crystallised from glacial acetic acid, from which solvent it separated in colourless needles melting at 291–292°. Bamberger and Schieffelin (*Ber.*, 1889, 22, 1377) gave 285° as the melting point of the diacetyl-*p*-diamine, and 245° as that of the diacetyl-*o*-diamine of the tetrahydronaphthalene series. The diamine obtained is in all probability the para-compound, for on oxidising a solution of its hydrochloride with warm chromic acid solution a quinone was produced; this substance was extracted with ether, the solvent evaporated, and the somewhat tarry residue extracted with light petroleum. The solution yielded yellow leaflets having the odour of benzoquinone and melting at 51°. These crystals were sublimed between watch glasses, when the quinone was obtained as a sublimate consisting of light yellow needles melting at 52–53°; the amount of material at our disposal did not admit of further purification. The melting point of tetrahydronaphthaquinone is given by Bamberger and Lengfeld as 55.5°.

A comparative reduction experiment carried out on  $\alpha$ -naphthylamine-4-azobenzene-4'-sulphonic acid confirmed the results previously obtained by Griess (*Ber.*, 1882, 15, 2192), the diamine extracted in the foregoing manner crystallised from light petroleum in grey needles and melted at 118–119°; the melting point of

naphthylene-1:4-diamine is given as  $120^{\circ}$ . The ethereal extract, when treated with acetic anhydride, yielded a precipitate of the diacetyl derivative which, after crystallisation from glacial acetic acid, separated in lenticular plates and melted at  $302-303^{\circ}$ , this being the melting point of the diacetyl derivative of the 1:4-diamine.

*ar-Tetrahydro- $\alpha$ -naphthylamine-4-sulphonic Acid,*  
 $\text{NH}_2 \cdot \text{C}_{10}\text{H}_9 \cdot \text{SO}_3\text{H}, \text{H}_2\text{O}.$

A mixture of 4 parts of *ar*-tetrahydro- $\alpha$ -naphthylamine and 5 parts of ordinary concentrated sulphuric acid were maintained at  $160-170^{\circ}$  until the dark liquid became viscid, the time required being about 30 minutes; the product was then stirred into crushed ice, the precipitated sulphonic acid being collected at the pump and washed free from sulphuric acid. A portion was crystallised from hot water, in which it is moderately soluble, the saturated solution being decolorised with animal charcoal; the acid separated from the cooled filtrate in colourless, transparent, acicular prisms which gradually assumed a pink tinge. An air-dried specimen was employed in the following analysis:

0.4264 gave 21.5 c.c. moist nitrogen at  $17^{\circ}$  and 740 mm.  $\text{N} = 5.69$ .

0.2138 „ 0.2039  $\text{BaSO}_4$ .  $\text{S} = 13.09$ .

0.6821, when dried for 5 hours at  $110^{\circ}$ , lost 0.050.  $\text{H}_2\text{O} = 7.34$ .

$\text{C}_{10}\text{H}_9\text{O}_3\text{NS}, \text{H}_2\text{O}$  requires  $\text{N} = 5.71$ ;  $\text{S} = 13.06$ ;  $\text{H}_2\text{O} = 7.34$  per cent.

The sulphonation was also effected with fuming acid containing 10 per cent. of sulphur trioxide, but no advantage is gained by the use of the stronger acid.

A portion of the sulphonic acid was suspended in warm water, treated with barium carbonate until effervescence ceased, and the filtered solution evaporated to small bulk, when the barium salt slowly separated in light brown, crystalline crusts. The analytical results for this salt were not satisfactory, but approximated to the composition of a salt  $\text{Ba}(\text{C}_{10}\text{H}_9\text{NSO}_3)_2, 3\text{H}_2\text{O}$ . The substance was accordingly converted into the sodium salt by the action of the calculated amount of sodium carbonate. The solution of the sodium amino-sulphonate after filtration from barium carbonate was carefully concentrated until crystallisation commenced. Analysis corresponded approximately with the formula  $\text{NH}_2 \cdot \text{C}_{10}\text{H}_9 \cdot \text{SO}_3\text{Na}, 2\text{H}_2\text{O}$ , but the salt was not obtained in a high state of purity.

*Diazotetrahydronaphthalene-4-sulphonic Acid.*

Four grams of the preceding aminosulphonic acid dissolved in a cold aqueous solution of sodium carbonate ( $\frac{1}{2}$  mol.) were treated suc-

cessively with 6.3 c.c. of concentrated hydrochloric acid and 1.3 grams of sodium nitrite (in 20 per cent. solution); the small, colourless crystals of the reprecipitated sulphonic acid were rapidly transferred into the opaque crystals of the diazo-compound which were collected at the pump. When freshly prepared, this diazo-acid gives a brilliant red, soluble azo-compound with sodium  $\beta$ -naphthol-3:6-disulphonate (R-salt), but when dried for several days on porous tile it loses this property and apparently undergoes some decomposition. Its reactions were accordingly studied in the moist condition. It closely resembles diazobenzenesulphonic acid, forming with  $\beta$ -naphthol an azo-colouring matter having tinctorial properties resembling those of naphthol-orange; with dimethylaniline, it yields a soluble aminoazo-compound which exhibits towards acids and alkalis the colour changes characteristic of methyl-orange. The former of the azo-compounds is produced in the ordinary way in aqueous solution, the formation of the latter takes place most readily in dilute alcohol.

*Tetrahydronaphthalene-1-sulphonic Acid from ar-Tetrahydro- $\alpha$ -naphthylamine-4-sulphonic Acid.*

The foregoing diazosulphonic acid, mixed into a paste with water, was slowly added to a cold solution of stannous chloride in equal volumes of water and concentrated hydrochloric acid; a thick, white precipitate of the corresponding hydrazo-compound was produced, the reaction being accompanied by a slight amount of frothing. The product, which was collected and washed with cold water, no longer gave an azo-colour with "R-salt," but reduced Fehling's solution even in the cold; it was then boiled with 20 per cent. copper sulphate until the blue coloration was permanent. The cuprous oxide was removed, the filtrate treated successively with hydrogen sulphide to eliminate copper, and with barium carbonate to remove sulphuric acid. The final filtrate, when concentrated considerably, yielded nodular crystals of *barium tetrahydronaphthalene-1-sulphonate*.

0.3378, when dried for  $2\frac{1}{2}$  hours at  $110^\circ$ , lost 0.0304.  $\text{H}_2\text{O} = 9.01$ .

$\text{Ba}(\text{C}_{10}\text{H}_{11}\text{SO}_3)_2 \cdot 3\text{H}_2\text{O}$  requires  $\text{H}_2\text{O} = 8.81$  per cent.

0.3076 (anhydrous salt) gave 0.1260  $\text{BaSO}_4$ .  $\text{Ba} = 24.08$ .

$\text{C}_{20}\text{H}_{22}\text{O}_6\text{S}_2\text{Ba}$  requires  $\text{Ba} = 24.50$  per cent.

*Tetrahydronaphthalene-1-sulphonic chloride*,  $\text{C}_{10}\text{H}_{11}\cdot\text{SO}_2\text{Cl}$ , was prepared by mixing the preceding barium salt with excess of phosphorus pentachloride, adding the product to cold water, and extracting the insoluble residue with light petroleum. The petroleum extracts yielded the sulphonic chloride in transparent, colourless plates melting at  $70.5^\circ$ . After hydrolysis with aqueous caustic potash:

0.1531 gave 0.095 AgCl. Cl = 15.35.

$C_{10}H_{11}O_2ClS$  requires Cl = 15.45 per cent.

A specimen of sodium naphthalene- $\alpha$ -sulphonate was likewise converted into sulphonic chloride, and the latter, after crystallisation from light petroleum, melted at 68—69° and depressed the melting point of the foregoing chloride to 45—47°, this result showing that in the sulphonation of *ar*-tetrahydro- $\alpha$ -naphthylamine, and in the subsequent reactions employed in the preparation of the sulphonic chloride, the hydrogenated nucleus does not lose its additional hydrogen atoms.

*Tetrahydronaphthalene-1-sulphonanilide*,  $C_{10}H_{11} \cdot SO_2 \cdot NH \cdot C_6H_5$ , produced on mixing warm ethereal solutions of aniline and the tetrahydronaphthalene-1-sulphonic chloride, is sparingly soluble in light petroleum, and separates in transparent, acicular crystals; it dissolves more readily in methyl alcohol, crystallising from this solvent in massive, transparent, vitreous prisms melting at 144—145°.

0.0518 gave 2.3 c.c. moist nitrogen at 16° and 767 mm. N = 5.21.

$C_{17}H_{17}O_2NS$  requires N = 4.90 per cent.

*Tetrahydronaphthalene-1-sulphonic Acid from ar-Tetrahydro- $\alpha$ -naphthylamine.*

*Tetrahydronaphthalene-1-sulphinic acid*,  $C_{10}H_{11} \cdot SO_2H$ .—Thirty grams of *ar*-tetrahydro- $\alpha$ -naphthylamine were dissolved in 150 grams of concentrated sulphuric acid and 450 c.c. of hot water, the solution rapidly cooled to -3°, and treated with 15 grams of sodium nitrite in 20 per cent. solution. The cooled mixture was rapidly filtered and thoroughly saturated with sulphur dioxide, copper powder made into a paste with water being then added. The sulphinic acid, which was partly dissolved and partly mixed with the copper precipitate, was extracted with ether, removed from the ethereal extract by means of aqueous sodium carbonate, and reprecipitated from the solution by dilute sulphuric acid. A portion was crystallised from water containing a little sulphurous acid, when it separated in colourless needles decomposing at 103—105°. The remainder (16.5 grams) was dissolved in aqueous caustic potash and the warm solution treated with 300 c.c. of 2 per cent. potassium permanganate; a little alcohol was added to reduce the excess of oxidising agent, the manganese oxides filtered off, and the filtrate evaporated to dryness.

A portion of the crude potassium salt was recrystallised and then dried at 150°, the anhydrous salt being analysed:

0.0857 gave 0.0292  $K_2SO_4$ . K = 15.28.

$C_{10}H_{11}O_3SK$  requires K = 15.60 per cent.

The remainder of the salt was converted into sulphonic chloride, the latter crystallising from light petroleum (b. p. 40—55°) in plates melting at 70·5°.

A portion was hydrolysed with aqueous caustic potash.

0·1688 gave 0·1035 AgCl. Cl = 15·16.

$C_{10}H_{11}O_2ClS$  requires Cl = 15·41 per cent.

This preparation did not depress the melting point of the sulphonic chloride obtained from *ar*-tetrahydro-*a*-naphthylamine-4-sulphonic acid after eliminating the amino-group.

A portion of the sulphonic chloride was converted into anilide, which crystallised from methyl alcohol in hard, transparent prisms with pyramidal or truncated terminations; it melted at 144—145° and did not depress the melting point of the anilide obtained in the manner indicated on p. 757.

*Action of p-Nitrobenzenediazonium Chloride on ar-Tetrahydro-a-naphthylamine-4-sulphonic Acid.*

A solution of *p*-nitrobenzenediazonium chloride prepared in the ordinary way was slowly added to a dilute aqueous solution of sodium tetrahydro-*a*-naphthylamine-4-sulphonate, a brownish-yellow precipitate separated which was filtered with some difficulty and could not be obtained crystalline. With alcoholic potash, it developed a deep purple coloration, in this respect resembling the other diazoamines derived from *p* nitroaniline. It was shown to contain diazo-nitrogen by heating with mineral acid contained in a flask fitted with an apparatus for measuring the gas evolved (compare Cain and Nicol, Trans., 1902, 81, 1412). About half a gram of the air-dried substance, when treated in this way with 50 per cent. sulphuric acid on the water-bath for 1 hour, evolved 6 per cent. of nitrogen, whereas the amount calculated from the formula  $NO_2 \cdot C_6H_4 \cdot N_2 \cdot NH \cdot C_{10}H_{10} \cdot SO_3H$  should be 7·03 per cent. As the specimen was by no means pure, and probably contained some unchanged aminosulphonic acid, this result indicates that the chief product of the action of a diazonium salt on *ar*-tetrahydro-*a*-naphthylamine-4-sulphonic acid is a diazoamine and not an aminoazo-compound.

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LXXVI.—*The Action of Nitrosyl Chloride on Pinene.*

By WILLIAM AUGUSTUS TILDEN.

*Preparation of Pinene Nitrosochloride.*

IN the paper (J. Chem. Soc., N. S., 1877, 15, 554) in which, in conjunction with Mr. Shenstone, I first described the application of nitrosyl chloride to the purpose of classifying the terpenes, attention was drawn to the apparent connection between the optical activity of the hydrocarbon operated on and the yield of nitrosochloride. It was found that terpenes of high rotatory power gave a much smaller product than others apparently identical in other respects, but having less action on the polarised ray. Von Baeyer having shown (*Ber.*, 1895, 28, 648) that pinene nitrosochloride is a bimolecular compound with the formula  $(C_{10}H_{16} \cdot NOCl)_2$ , it occurred to me that the inferior yield of nitrosochloride by the more strongly rotating varieties of the hydrocarbon was due to the destructive effect of heat generated in the process of inversion of one-half of the compound as soon as formed, and that by using a mixture of *d*- and *l*-pinenes in due proportions the bimolecular compound would at once be produced by simple combination of the two semi-molecules without further change in either of them, and a larger product would result. This turns out to be the case.

When to pinene from American turpentine, diluted with half its volume of chloroform and cooled to about  $0^\circ$ , is added very gradually a solution of nitrosyl chloride in chloroform, an intense blue coloration is observed on the addition of each drop of the reagent. The colour quickly fades and a white, crystalline precipitate soon begins to form. A similar, though less intense, blue colour is produced when ethyl or amyl nitrite together with hydrochloric acid is employed, as in the process introduced by Wallach (*Annalen*, 1888, 245, 251). When the blue colour is no longer produced, the liquid diluted with about three times its volume of 84 per cent. alcohol yields a precipitate which, after being washed with alcohol and dried at about  $50^\circ$ , amounted in a series of experiments pretty uniformly to 31—32 per cent. of the pinene. The specimen used had a rotation of about  $+7^\circ$  in a 200 mm. tube.

When the *d*-pinene was replaced by *l*-pinene of greater rotatory power ( $-57^\circ 48'$  in 200 mm.), the yield was much less and never exceeded 20 per cent. of the pinene employed.

A specimen of pinene from the turpentine of *Pinus Khasyana*, which has a specially high rotatory power ( $+80^\circ 41'$  in 200 mm.), and probably

consists of nearly pure *d*-pinene, was then tried. The amount of nitrosochloride it could be made to yield was only 5.5 per cent. These results confirm the impressions derived from the experiments made in 1877.

An experiment was then made on an optically inactive mixture of the two last-named varieties of pinene, and it was found by the same process to yield 55.6 per cent. of its weight of nitrosochloride. When, in the process described, light petroleum is substituted for chloroform, no blue colour is at first produced on the addition of the nitrosyl chloride, and the yield of nitrosochloride is much smaller, but, with a view to economy, petroleum may be used in place of a portion of the chloroform. The process preferred is therefore as follows:

The pinene from ordinary American turpentine has usually a rotatory power about one-third of that of the corresponding hydrocarbon from French turpentine, but in consequence of the variation in different samples of these liquids it is necessary to distil from the commercial oils of turpentine the fraction boiling at 156—160°, to determine its rotatory power, and to mix the two liquids in exactly corresponding proportions. This inactive mixture of pinenes is then diluted with about two-thirds of its volume of petroleum (boiling at about 90—100°) and cooled to a few degrees below 0°. A solution of nitrosyl chloride in a mixture of equal volumes of chloroform and petroleum, saturated at 0° (which contains about 8 per cent. of its weight of NOCl), is then allowed to drop slowly from a tap-funnel into the liquid, which is kept in motion by a mechanical stirrer. The temperature should not be allowed to rise much above 0°. A green colour is at first developed, but this becomes bluer in shade as the chloroform accumulates in the mixture, and a white precipitate is soon copiously produced. The nitrosyl chloride is ultimately added in decided excess, and a quantity of alcohol is then added, equal to about  $1\frac{1}{2}$  times the total volume of the mixed liquids, and the whole left in the ice for half an hour. The precipitate is then collected at the pump, washed with alcohol, and dried, first by exposure to the air, then at about 50°.

The process in which amyl nitrite is mixed with the pinene diluted with glacial acetic acid and hydrochloric acid is allowed to drop into the cooled mixture is very convenient, but less productive. In my hands, using the same mixture of pinenes, it yielded only about 33 per cent. of the pinene employed. This appears to be explained by the fact that the theoretical amount of hydrochloric acid cannot be added without causing decomposition. The temperature can be kept below 0° without difficulty until about half the amount of acid has been introduced; effervescence then sets in, attended by a rapid rise of temperature.

In the course of trying variations of my process, one experiment led to a result which helps to explain this effect. Pinene was diluted with

three volumes of petroleum, and, with the object of avoiding the separate preparation of a solution of nitrosyl chloride, the gas was passed into a small quantity of ordinary strong hydrochloric acid, upon which the hydrocarbon floated as a separate layer. The whole was cooled below  $0^{\circ}$  and a white precipitate soon made its appearance. Ultimately a quantity of nitrosochloride corresponding with 14 per cent. of the pinene was collected. The aqueous acid became syrupy, and when diluted with a mixture of alcohol and water it gave a copious crystalline precipitate which, when collected, represented about one-third of the weight of the pinene, while a further quantity remained in the mother liquors. After recrystallisation from methyl alcohol, this compound was recognised as *i*-carvoxime hydrochloride (m. p.  $127-128^{\circ}$ ). Von Baeyer has observed that pinene nitrosochloride is changed into this compound by contact for three days with an ethereal solution of hydrogen chloride. In the circumstances described, however, the conversion is immediate.

In the process for the production of pinene nitrosochloride, the employment of aqueous hydrochloric acid appears to give rise to the same change. The effervescence which occurs can be accounted for by the hydrolysis of the carvoxime, whereby hydroxylamine is formed, which is immediately destroyed by the nitrosyl chloride with evolution of nitrous oxide.

#### *Properties of Pinene Nitrosochloride.*

The original statement (Tilden and Shenstone, J. Chem. Soc., N. S., 1877, 15, 556, and Wallach, *Annalen*, 1888, 245, 252) that the melting point of the nitrosochloride is  $103^{\circ}$  is incorrect. The fusion is accompanied by decomposition, and the temperature at which it occurs varies a little according to circumstances. The melting point of this compound when well washed with alcohol and thoroughly dried, but not recrystallised, is usually  $109-111^{\circ}$ . After recrystallisation from chloroform, it reaches  $115^{\circ}$ . The same compound is produced by the employment of inactive pinene regenerated from the nitrosochloride, as described later.

From whatever hydrocarbon prepared, the solution of the nitrosochloride in chloroform is optically inactive. It may be recrystallised from chloroform either by allowing the solution to evaporate at the temperature of the air, or by the addition of alcohol. It is advisable not to operate on more than a few grams at a time, and to avoid the application of heat. Fifty grams mixed with 250 c.c. of chloroform very gently warmed developed so much heat as to cause the liquid to boil, and, although cooled as quickly as possible, the whole was decomposed. The solution yielded on evaporation a red resin, together with a considerable quantity of nitrosopinene (m. p.  $129^{\circ}$ ).

If pure pinene nitrosochloride dissolved in chloroform is diluted with alcohol, the solution in a few hours assumes the orange-red colour developed in the mother liquors obtained in the ordinary process of preparation. This solution reduces Fehling's solution freely, and evidently contains hydroxylamine.

*Nitrosopinene and Pinyllamine.*

As the nitrosochloride is undoubtedly formed by the union of a dextro- and a lævo-compound, it seemed probable that nitrosopinene, which is produced from it by removal of  $2\text{HCl}$  and is monomolecular, might exist in two forms. Attention was long ago (J. Chem. Soc., N. S., 1877, 15, 557) drawn to the peculiarity of habit exhibited by the nitroso-compound prepared from certain specimens of *l*-pinene. Recent experiments, however, prove that when this variety is mixed with the same compound prepared from *d*-pinene, the melting point is not depressed, and that when the two varieties are dissolved in aqueous caustic soda, reprecipitated by acetic acid, and recrystallised from alcohol, both yield crystals of the same form as described by Maskeleyne (J. Chem. Soc., N. S., 1875, 13, 518). The nitrosopinene derived from *l*-pinene therefore probably owes the peculiarity originally observed to the presence of a trace of some unknown impurity.

Whether obtained from *d*- or from *l*-pinene, however, the crystals of nitrosopinene consist of a mixture of prisms which exhibit hemihedrism. I am indebted to Miss M. A. Whiteley, D.Sc., for kindly undertaking the task of separating a quantity of the *r*- and *l*-forms. The solution of one of them in alcohol was, however, optically inactive. Pinene benzylnitrolamine shows a similar phenomenon (Hintze, *Annalen*, 1889, 252, 131. See also Pope, *Trans.*, 1896, 69, 971, and Clare de Brereton Evans, *Trans.*, 1897, 71, 525 and 1001).

As it seemed hopeless to attempt the resolution of nitrosopinene into optically active isomerides by any process of crystallisation, it was reduced to pinyllamine and the base converted into its salts with optically active strong acids.

Reychler's *d*-camphorsulphonic acid and the *l*-oxime of the same and *d*-bromocamphorsulphonic acid, for which I am indebted to Professor Pope, were used. The camphorsulphonate was crystallised repeatedly from ethyl acetate. In another experiment, about  $2\frac{1}{2}$  molecules of pinyllamine nitrate were dissolved in water together with one molecule of ammonium camphorsulphonate, and advantage was taken of the slight solubility of pinyllamine nitrate to precipitate the base from the mixture in successive portions, leaving the elements of pinyllamine camphorsulphonate in solution.

The pinylamine *d*-bromocamphorsulphonate was recrystallised fractionally many times, first from ethyl acetate, and in another series of experiments from acetone. The base was in each case recovered from the most soluble and least soluble portions respectively, converted into hydrochloride and examined in the polarimeter, but no optical activity could be detected. As no formula has yet been proposed which will account for the disappearance of asymmetry from the molecule, ordinary pinylamine must still be regarded as probably consisting of a mixture of optical isomerides, notwithstanding that these attempts to resolve it have been unsuccessful.

*Action of Bases on Pinene Nitrosochloride.*

Wallach has already shown that primary fatty bases and benzylamine yield nitrolamines, but that aniline acting on the nitrosochloride regenerates pinene and forms aminoazobenzene. I have several times repeated this experiment, and find that the interaction with aniline proceeds slowly but completely in the cold, yielding the same products. The yield of pinene is, however, always small. I have found that methylaniline is a more advantageous reagent. Pinene nitrosochloride, heated gently together with two molecular proportions of methylaniline, diluted with about three times its volume of alcohol, dissolves quietly without any sign of the violent action which occurs when aniline is used. A slight excess of acetic acid may then be added and the liquid distilled in steam. The pinene separated from the first portions of the distillate, dried with caustic potash and distilled, amounts to about 63 per cent. of the theoretical quantity. The latter stage of the steam distillation gives phenylmethylnitrosoamine as the chief secondary product, a small quantity of a purple base remaining in the residue.

Dimethylaniline tried in similar proportions gave about the same yield of pinene. There was no spontaneous heating or evolution of gas, but the liquid assumed an intense green colour. This is due to the formation of the green hydrochloride of a purple base which gives Liebermann's reaction freely, and is not *p*-nitrosodimethylaniline.

Dimethyl-*p*-toluidine gave a similar result; the base formed gave Liebermann's reaction, but in this case no green colour was produced, the liquid assuming a deep yellow tint.

Pyridine behaves in a different way. In alcoholic solution, it produces no pinene, but only viscid products; in chloroform, it fixes hydrogen chloride and produces nitrosopinene.

The inactive pinene recovered by either of these operations from the nitrosochloride is very readily reconverted into that compound by the process I have described. It yields uniformly 55 per cent. of its

weight of nitrosochloride, an amount which is practically identical with the product obtained, as already stated, from an inactive mixture of *d*- and *l*-pinenes.

*Theoretical.*

The course of the action of nitrosyl chloride on pinene consists in the formation first of a simple nitrosochloride which, in solution, in common with nitroso-compounds in general, exhibits a blue colour. The union of two such molecules (*d* and *l*) gives rise to the colourless bimolecular or racemic compound  $(C_{10}H_{16} \cdot NOCl)_2$ , which, from its reactions with aromatic bases, evidently contains the elements of the chloride corresponding with nitrous acid.

The two semi-molecules are supposed by von Baeyer to be linked together by the two NO groups, which must be united by pentadic nitrogen,  $\begin{smallmatrix} \text{N} & \text{N} \\ | & | \\ \text{O} & \text{O} \end{smallmatrix}$ . This probably accounts for the disappearance of the blue colour when the compound is formed. Certain of the nitrolamines formed from the nitrosochloride by substitution of the basic residue for the chlorine are also stated by von Baeyer to be bimolecular.

Pinene benzylnitrolamine gave in my laboratory by the cryoscopic method the value 371 for the molecular weight, whilst the formula  $C_{10}H_{16} \cdot NO \cdot NH \cdot C_7H_7$  corresponds with 272.

On the other hand, the piperidylnitrolamine gave in one series of experiments 215, 209, and 214 as the value of the molecular weight. A second specimen gave 196 and 212. The simple formula  $C_{10}H_{16} \cdot NO \cdot NC_5H_{10}$  corresponds with 250.

Determinations of the molecular weight of the nitrosocyanide (Tilden and Burrows, Proc., 1902, 18, 161) gave 188 and 189, the formula  $C_{10}H_{16} \cdot NO \cdot CN$  requiring 192.

Hence it appears that when in the nitrosochloride the chlorine is replaced by cyanogen or by the piperidine residue, the compound becomes monomolecular and reacts as an oxime. The chlorine in the nitrosochloride therefore controls the hydrogen of the secondary carbon to which the NO group is attached, preventing the formation of the isonitroso-compound.

LXXVII.—*The Comparison of the Rotation-values of Methyl, Ethyl, and n-Propyl Tartrates at Different Temperatures.*

By THOMAS STEWART PATTERSON.

I HAVE recently had occasion to examine the rotations of methyl, ethyl, and *n*-propyl tartrates, and as the figures for these substances with reference to change of temperature present some features of interest, it seems worth while to collect the data here and briefly discuss them.

*Methyl Tartrate.*

Values for the rotation of methyl tartrate were given in a former paper (Trans., 1901, 79, 280), but the specimen used, owing to its method of preparation, was apparently contaminated either with ethyl tartrate or methyl ethyl tartrate, since the numbers given are consistently too high, as was noticed when the rotation of a fresh specimen, which had been carefully prepared and purified, was determined.

When methyl tartrate is first prepared, it is usually difficult to induce it to crystallise at all, although it may be pure so far as can be judged by its rotation or density. Indeed, for optical experiments, it is rather an advantage that it should remain liquid. When it does happen to solidify, however, it melts at 48·5—49° and can be crystallised repeatedly from benzene without any alteration of melting point. The specimen, the rotation values of which are given in the paper already cited, was prepared from ethyl tartrate by the action of methyl alcohol and hydrogen chloride, and was found to melt at 55—56°, although there was no doubt from the rotation and density that the substance was methyl tartrate.

The fresh preparation for which data are given below was made from the acid by the method of saturation with hydrogen chloride; it was distilled under diminished pressure, dissolved, when liquid, in benzene, and made to crystallise by adding a very small quantity of a specimen, the melting point of which was originally 55—56°, but which, when redetermined a year or more later, had risen to 59°. The crystals obtained were carefully dried and then redistilled under diminished pressure. The substance thus obtained melted at 61·5°, this value remaining unchanged after further crystallisation from

benzene. It may be noted too that methyl tartrate having this melting point can be crystallised from water. A specimen of methyl tartrate melting at  $48^{\circ}$  was fused on a watch glass and allowed to cool; a very minute crystal of the less fusible variety was added and stirred in with a glass rod. This caused the immediate separation of a solid, the melting point of which was  $61^{\circ}$ .

It thus appears that there are two solid forms of methyl tartrate, one of which melts at  $48^{\circ}$  and the other at  $61.5^{\circ}$ , the former, unstable, variety, as ought to be the case, being much more easily soluble in water and benzene than the latter.

The following table gives the rotation data for methyl tartrate melting at  $61.5^{\circ}$ , prepared in the foregoing manner. It solidified readily after having been fused, so that it was a little difficult to determine its rotation at the lower temperatures recorded.

*Rotation of Methyl Tartrate.*

Temperature.	$\alpha_D^{25}$ (100 mm.).	Sp. gr.	$[\alpha]_D^{25}$ .	$[M]_D^{25}$ .
$16.8^{\circ}$	$+2.456^{\circ}$	1.3386	$+1.83^{\circ}$	$+3.27^{\circ}$
20	—	—	$2.07^*$	$3.68^*$
27.8	3.503	1.3268	2.64	4.70
40.8	4.723	1.3130	3.60	6.41
52.3	5.720	1.3007	4.40	7.83
61.6	6.100	1.2908	4.72	8.41
71.6	6.702	1.2805	5.23	9.32
99	7.702	1.2515	6.15	10.96
100	—	—	$6.18^{\dagger}$	$11.00^{\dagger}$

Temperature .....	$18.25^{\circ}$	$42.4^{\circ}$	$60.35^{\circ}$	$77.3^{\circ}$
Sp. gr. observed .....	1.3370	1.3122	1.2925	1.2745

\* Interpolated.

† Extrapolated.

The curve for methyl tartrate in the figure on p. 768 has been drawn from these data. It represents the variation of molecular rotation with change of temperature, and will be referred to in the sequel.

*Ethyl Tartrate.*

Data for the specific rotation of this substance have already been given in a previous paper (Trans., 1901, 79, 198), and from them the following values of molecular rotation have been calculated.

Temperature.	$[M]_D^{25}$ .	Temperature.	$[M]_D^{25}$ .
10.8°	+ 13.66°	46.1°	+ 21.10°
11.3	13.72	55.1	22.54
16	14.85	67.2	24.21
20.1	15.80	77.1	25.34
25.1	16.99	84.4	26.22
29.9	17.92	89.4	26.72
33.7	18.74	100	27.75
37.6	19.69		

The curve obtained from these data is also shown in the figure on p. 768.

#### *n*-Propyl Tartrate.

The *n*-propyl tartrate used in these experiments was prepared by mixing together tartaric acid and *n*-propyl alcohol in the proportion of one molecule to four, heating to about 70°, and passing in hydrogen chloride until all the acid had dissolved. The mixture was then allowed to cool, saturated with hydrogen chloride and the alcohol distilled off under diminished pressure. Fresh alcohol was added, saturation with hydrogen chloride repeated, the *n*-propyl tartrate distilled under diminished pressure and twice redistilled. It boiled at 171—172° (temp. of bath, 194—205°) under 17 mm. pressure.

#### *Rotation of n*-Propyl Tartrate.

Temperature.	$\alpha_D^{25}$ (66.04 mm.).	Sp. gr.	$[\alpha]_D^{25}$ .	$[M]_D^{25}$ .
17°	+ 9.330°	1.1403	+ 12.39°	+ 29.02°
20	—	—	12.67*	29.67*
27.7	9.997	1.1300	13.40	31.38
45.6	10.908	1.1127	14.84	34.75
62.3	11.463	1.0968	15.82	37.05
98.5	12.123	1.0620	17.28	40.47
100	—	—	17.35†	40.6†

Temperature .....	18.05°	39.75°	57.45°	77.96°
Sp. gr. observed.....	1.1394	1.1185	1.1013	1.0819

\* Interpolated.

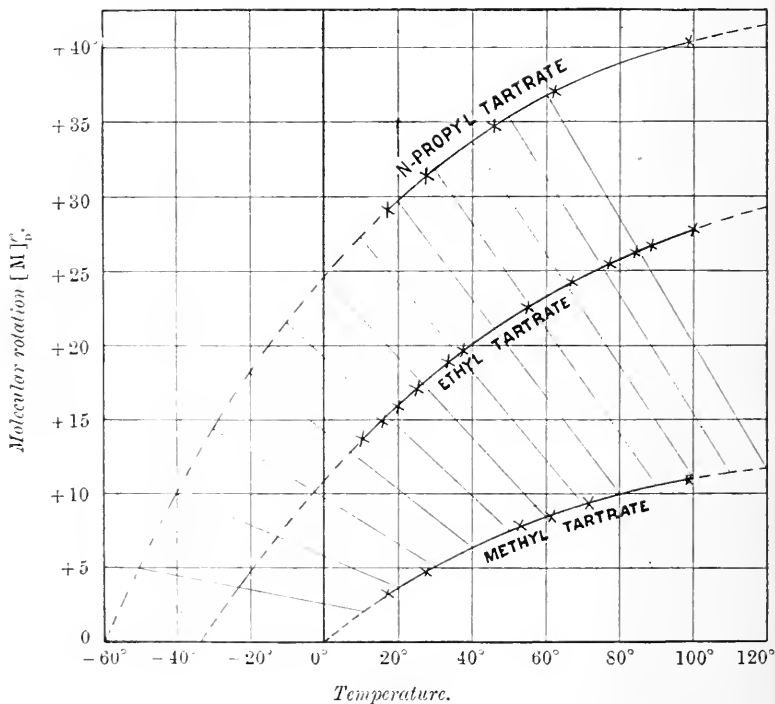
† Extrapolated.

Pictet (*Arch. phys. Nat.*, 1882, [iii], 7, 82) gives  $[\alpha]_D^{20} + 12.44^\circ$  and  $[\alpha]_D^{100} + 17.11^\circ$ , so that his preparation does not seem to have been so pure as that with which the above determinations were made.

The curve obtained from these data is also shown in the following figure.

*Comparison of Rotation Values.*

Passing now to a general consideration of these curves, we may, to begin with, confine our attention to the parts represented by full lines which cover the points experimentally determined. The rotations of these three substances all increase with rise of temperature, the gradient being greater at low temperatures than at higher ones. The increase in rotation, however, is neither the same nor regular. Thus the change in rotation of methyl tartrate between  $0^{\circ}$  and  $100^{\circ}$  is  $11^{\circ}$ , of ethyl

*Molecular rotations of methyl, ethyl, and n-propyl tartrates.*

tartrate  $16.9^{\circ}$ , and of *n*-propyl tartrate only  $15.85^{\circ}$ , whereas it might have been expected that in this respect, as in many others, the behaviour of ethyl tartrate would be intermediate between those of the methyl and *n*-propyl compounds.

Comparison of the rotations in other directions is no more satisfactory, as is at once seen when any attempt is made to discover quantitative regularities amongst the data obtained. This is obviously due to the great influence which change of temperature exerts in modifying the

rotations of the esters, and we are thus confronted with a problem of the first importance. At what temperatures may optically active substances be considered as comparable with each other as regards their rotation?

For many years the influence of change of temperature was almost completely ignored, and even at the present time rotation values are often stated without reference to this factor and in such a manner as to be quite useless for any purpose other than that immediately in hand. The importance of this variable having, however, been recognised, it is most natural as a first approximation to institute comparisons between the rotations of different compounds, the constants of which are all taken at one and the same temperature, but it should be carefully noticed that this convention is only adopted for want of some more satisfactory suggestion. Comparisons made under these circumstances—and a considerable number of data now exist for the purpose—tend chiefly to show that we have not yet hit upon the proper conditions for the discovery of regularities of any general application. This may be demonstrated by means of the following tables, the first of which gives the rotation values of the three esters at a number of different temperatures.

TABLE I.

	0°.	20°.	40°.	60°.	80°.	100°.	120°.
<i>n</i> -Propyl tartrate $[M]_D^{20} \dots$	24.65	29.66	33.73	36.80	38.97	40.57	41.65
Ethyl        ,,       ,, ...	10.80	15.95	20.00	23.25	25.80	27.70	29.20
Methyl       ,,       ,, ...	0.0	3.68	6.41	8.40	9.85	11.00	11.6

Amongst these figures we may institute, for illustration, several comparisons. By determining the ratio between the rotations of *n*-propyl and methyl tartrates, we obtain the following numbers:

TABLE II.

*Ratios of Rotations of n-Propyl and Methyl Tartrates.*

Temperature .....	0°	20°	40°	60°	80°	100°	120°
Ratio .....	$\infty$	8.06	5.26	4.38	3.96	3.69	3.58

Comparing the rotations of methyl and ethyl tartrates we have:

TABLE III.

*Ratio of Rotations of Ethyl and Methyl Tartrates.*

Temperature .....	0°	20°	40°	60°	80°	100°	120°
Ratio .....	$\infty$	4.33	3.12	2.77	2.62	2.52	2.51

For *n*-propyl and ethyl tartrates we find:

TABLE IV.

*Ratio of Rotations of n-Propyl and Ethyl Tartrates.*

Temperature .....	0°	20°	40°	60°	80°	100°	120°
Ratio .....	2.28	1.86	1.69	1.58	1.51	1.46	1.43

The above data are sufficient to show that the temperature at which any comparison of the rotations of active compounds is made is of fundamental importance, and that although some peculiarity might easily be discovered at one temperature, but little weight can be attached to it, since it is almost certain to disappear completely at some other temperature. Thus, whilst the rotation of *n*-propyl tartrate at 0° is 2.28 times as great as that of ethyl tartrate at the same temperature, it is only 1.43 times as great at 120°, the ratios in the other cases varying between much wider limits.

No greater constancy is found if, instead of seeking for a connection between the rotation values themselves, the differences between them are compared. This is shown in the following table, in which the upper line gives the differences ( $\Delta_1$ ) between the rotations of *n*-propyl and ethyl tartrates at the temperatures shown, whilst the lower one gives the differences ( $\Delta_2$ ) between those of ethyl and methyl tartrates, the ratios (*R*) between these numbers being added.

TABLE V.

	0°.	<i>R.</i>	20°.	<i>R.</i>	40°.	<i>R.</i>	60°.	<i>R.</i>
$\Delta_1$ ...	13.85°		13.71°		13.73°		13.55°	
$\Delta_2$ ...	10.80	1.282	12.27	1.117	13.59	1.010	14.85	0.913
	80°.	<i>R.</i>	100°.	<i>R.</i>	120°.	<i>R.</i>		
$\Delta_1$ ...	13.17°		12.87°		12.45°			
$\Delta_2$ ...	15.95	0.826	16.70	0.771	17.55	0.709		

It will be noticed that here  $\Delta_1$  gradually diminishes, whilst  $\Delta_2$  increases, with rise of temperature; obviously, therefore, the ratio of the differences also becomes less. At 0° then and at any temperature up to 41°, the replacement of two methyl by two ethyl groups produces a greater change of rotation than the replacement of two ethyl by two *n*-propyl groups; at higher temperatures the opposite is the case, whilst at 41° the changes thus brought about are equal.

It will be clear from what has been said that before any quantitative connection can possibly be discovered between optical activity and chemical constitution, some method must be found of eliminating the disturbing influence of change of temperature. Relationships between the rotations of active substances, to be of value, must be independent of temperature, as would be the case were specific rotation really a

constant, as originally supposed. The convention of making comparisons at identical temperatures is the only one which has hitherto been tried. It is obviously very unsatisfactory, and it remains now to consider whether any suggestion leading to better results can be made.

We may set out from the axiom that satisfactory comparisons can only be instituted between the properties of substances which are in corresponding conditions, and since it must indeed be highly exceptional that two substances, other than perfect gases, can be comparable at the same temperature and pressure, the absence of regularities dealt with above is really not surprising. That the physical properties of chemical compounds are not generally comparable at the same temperature has of course been recognised for many years. Kopp took account of this fact when he showed that greater regularity could be discovered regarding molecular volume when the constants were determined at the respective boiling points of the compounds examined, rather than at one definite temperature, and this mode of comparison has received its justification and an extended application in the general form of van der Waals' equation. Whether, in point of rotation, optically active substances would be comparable at equal fractions of the critical constants, it is difficult to say. If the suggestion made below be correct, this would probably not be so, but, however that may be, since critical constants are not easily determined, it becomes necessary in the present instance to seek for some other criterion of correspondence, and a consideration of the diagram on p. 768 furnishes an idea which may be of importance in this connection.

It is obvious from the figure that the rotation of methyl tartrate would vanish at, or near,\*  $0^{\circ}$ , whilst below this temperature it would be negative. If now the ethyl tartrate curve is similarly continued towards the left, an extrapolated value can be found for the temperature at which its rotation also would disappear, but since the extrapolation has to be carried out through a greater distance than before, the value found will be correspondingly less exact, and doubtless liable to an error of several degrees. When the curve is drawn by the aid of a fairly long piece of steel held at the ends so as to avoid too sudden changes of curvature, it cuts the zero abscissa at a point corresponding with a temperature of  $-34^{\circ}$ , and this number has been adopted for the purposes of the following argument. In a similar way, the curve for *n*-propyl tartrate may be produced, and is found to cut the zero axis at  $-60^{\circ}$ , the probable error in this case being still greater than for ethyl tartrate. All three curves have also been extrapolated in the opposite direction up to  $120^{\circ}$ , which can be done with greater certainty.

\* Within one degree

We are not far wrong then in assuming that methyl tartrate becomes inactive at  $0^\circ$ , ethyl tartrate at  $-34^\circ$ , and *n*-propyl tartrate at  $-60^\circ$ ; these molecules, at the temperatures named, lose their asymmetry so far as it is revealed by its effect on polarised light,\* and in this we seem to find the required criterion. It appears rational and legitimate to assume that the molecules of the different substances at those temperatures at which their rotations vanish are in corresponding optical states, although this may not be the same thing as correspondence in the sense of van der Waals' equation, and this appears to be the solitary point which the subject presents for attack. Setting out then from the assumption that since methyl, ethyl, and *n*-propyl tartrates are inactive, and therefore in corresponding optical states, at  $0^\circ$ ,  $-34^\circ$ , and  $-60^\circ$  respectively, it may be assumed, as a first approximation, that the rotations of methyl tartrate at  $T^\circ$ , ethyl tartrate at  $(T-34^\circ)$ , and *n*-propyl tartrate at  $(T-60^\circ)$  are directly comparable.

The following tables, each of which is analogous to one of those previously referred to, give the results of comparisons based on this idea, but with a very slight modification.

The data in Table VI have been obtained by selecting points on the methyl tartrate curve  $10^\circ$  apart, from which lines have been drawn to intersect the *n*-propyl tartrate curve at temperatures  $60^\circ$  lower. These lines cut the ethyl tartrate curve, and the three points of intersection are assumed to correspond as regards temperature and rotation.

To follow the guiding idea completely, it would be necessary to select points on the ethyl tartrate curve exactly  $34^\circ$  below those taken on the methyl tartrate curve, but the above construction almost realises this; it gives, indeed, slightly better results, and is in the meantime quite as good a basis of calculation, inasmuch as the two fundamental temperatures for the ethyl and *n*-propyl esters are not accurately known.

TABLE VI.

	1.			2.		
	$t^\circ$ .	$\Delta_{t^\circ}$ .	$[M]_D^\circ$ .	$t^\circ$ .	$\Delta_{t^\circ}$ .	$[M]_D^\circ$ .
<i>n</i> -Propyl tartrate .....	$-50^\circ$	$26.7^\circ$	$5.10^\circ$	$-40^\circ$	$27^\circ$	$10.10^\circ$
Ethyl       ,, .....	$-23.3$	$33.3$	$3.75$	$-13$	$33$	$7.20$
Methyl     ,, .....	$+10$		$1.83$	$+20$		$3.68$
	3.			4.		
<i>n</i> -Propyl tartrate .....	$-30$	$27.3$	$14.4$	$-20$	$27$	$18.20$
Ethyl       ,, .....	$-2.7$	$32.7$	$10.20$	$+7$	$33$	$12.77$
Methyl     ,, .....	$+30$		$5.16$	$+40$		$6.41$

\* These temperatures only apply to yellow light.

TABLE VI. (*continued*).

5.				6.			
	$t^{\circ}$ .	$\Delta t^{\circ}$ .	$[M]_D^{\circ}$ .	$t^{\circ}$ .	$\Delta t^{\circ}$ .	$[M]_D^{\circ}$ .	
<i>n</i> -Propyl tartrate .....	-10	26.8	21.5	+0	26.7	24.65	
Ethyl „ .....	+16.8	33.2	15.23	+26.7	33.3	17.45	
Methyl „ .....	+50		7.50	+60		8.40	
7.				8.			
<i>n</i> -Propyl tartrate .....	+10	26.4	27.33	+20	26	29.66	
Ethyl „ .....	+36.4	33.6	19.35	+46	34	21.05	
Methyl „ .....	+70		9.20	+80		9.85	
9.				10.			
<i>n</i> -Propyl tartrate .....	+30	26	31.83	+40	25.7	33.73	
Ethyl „ .....	+56	34	22.65	+65.7	34.3	24.00	
Methyl „ .....	+90		10.45	+100		11.00	
11.				12.			
<i>n</i> -Propyl tartrate .....	+50	25.3	35.35	+60	25	36.80	
Ethyl „ .....	+75.3	34.7	25.20	+85	35	26.30	
Methyl „ .....	+110		11.35	+120		11.65	

In the above table, each group of figures is denoted by a numeral, and when any compound is cited as belonging to one of these groups the temperature stated must be understood. With regard to these data, attention may, in the first place, be directed to the temperature differences. The temperature difference for *n*-propyl and methyl tartrates is of course always 60°, whilst those between *n*-propyl and ethyl tartrates and between ethyl and methyl tartrates vary a little and are given in the  $\Delta t$  column. It must be noted that the numbers given in groups 1, 2, 3, and even in 4, since they are taken from the extrapolated parts of the *n*-propyl and ethyl tartrate curves, cannot claim the same accuracy as those in the later groups. Nevertheless,  $\Delta t$  varies only 2° in the groups 4 to 12, the mean values being 26° between the *n*-propyl and ethyl, and 34° between the ethyl and methyl compounds, so that the variation is only 1° on either side of the mean, which has thus the value we assumed as a starting point.

The increase of rotation which these three esters undergo between two given temperatures, namely, 0° and 100°, was shown on p. 769 to be irregular. Taking another similar example, we find that between 60° and 120° the rotation of methyl tartrate increases by 3.2°, whilst between the same temperatures the increase for ethyl tartrate is 6° and for *n*-propyl tartrate 4.8°. From what has been said above, however, it is probable that the change in rotation of methyl tartrate between 60° and 120° should be compared with the change in ethyl tartrate between 26.7° and 85° and with that in *n*-propyl tartrate between 0° and 60°, and the three increments between these corresponding temperatures, namely, 3.2°, 8.85°, and 12.15°, stand at least in the order which might *a priori* be expected.

Taking now the rotation ratios in order to compare them with those in Table II, we obtain :

TABLE VII.

*Ratios of Rotations of n-Propyl and Methyl Tartrates at Corresponding Temperatures.*

Group :	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.
Ratio :	2.79	2.74	2.79	2.84	2.87	2.93	2.97	3.01	3.05	3.07	3.11	3.16

It is obvious at once that this is a great improvement on Table II, in which the ratios varied from  $\infty$  to 3.58, and it would appear that when propyl and methyl tartrates are in corresponding optical conditions the rotation of the former is approximately 2.95 times that of the latter.

Comparing in the same manner the rotations of ethyl and methyl tartrates we obtain :

TABLE VIII.

*Ratios of Rotations of Ethyl and Methyl Tartrates at Corresponding Temperatures.*

Group :	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.
Ratio :	2.05	1.96	1.98	1.99	2.03	2.08	2.10	2.14	2.17	2.18	2.20	2.26

Here again there is only a slight alteration in the value of the ratio, and we may say that the rotation of ethyl tartrate is rather more than twice as great as that of methyl tartrate when the constants are taken at corresponding temperatures.

Again, comparing the rotation values of *n*-propyl and ethyl tartrates, we obtain :

TABLE IX.

*Ratios of Rotation of n-Propyl and Ethyl Tartrates at Corresponding Temperatures.*

Group :	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.
Ratio :	1.36	1.40	1.41	1.42	1.41	1.41	1.41	1.41	1.41	1.41	1.40	1.40

In this case, the agreement is still better, and at corresponding temperatures the rotation of *n*-propyl tartrate is 1.41 times that of ethyl tartrate.

Finally, we may examine the ratios of the differences of the rotations at corresponding temperatures for comparison with Table V. We obtain then,  $\Delta_1$  being the difference between the rotations of *n*-propyl and ethyl tartrates and  $\Delta_2$  that between the rotations of ethyl and methyl tartrates, and R being the ratio of  $\Delta_1$  to  $\Delta_2$ , the following :

TABLE X.

Group:	3.	R.	5.	R.	7.	R.	9.	R.	11.	R.
$\Delta_1$ .....	4.2	0.833	6.27	0.811	7.98	0.786	9.18	0.753	10.15	0.733
$\Delta_2$ .....	5.04		7.73		10.15		12.20		13.85	

In this case, the ratio does not remain quite constant, but the variation is much less than that shown in Table V, where the alteration was from 1.282 to 0.709 within the same range of temperature. The foregoing variation is also linear, and therefore might easily be allowed for if necessary.

It will doubtless be admitted from what has been said that the method of comparison suggested presents considerable advantages, and it is only necessary to draw attention to one other point in its favour. It has already been shown that when comparisons are made at identical temperatures the ratios of the rotations can have very various values, so that at  $0^\circ$  the ratios of the rotations of both *n*-propyl and ethyl tartrates to that of methyl tartrate will be positive and infinite, becoming negative at a slightly lower temperature; at  $-34^\circ$ , when the rotation of ethyl tartrate vanishes, the rotation of *n*-propyl tartrate is positive and infinitely great compared with that of the ethyl ester, whilst the rotation of methyl tartrate is negative and infinitely great compared with the same standard; at  $-60^\circ$ , the rotations of both methyl and ethyl tartrates are negative and infinitely great compared with that of *n*-propyl tartrate.

The method of comparison suggested above eliminates difficulties of this kind. The ratios which have been shown to exist at higher temperatures persist not only down to the point where all the rotations simultaneously become zero, but, since by taking corresponding temperatures all the rotations become negative at the same time and not one after another, they would presumably hold even for still lower temperatures.

It will also be noticed, if the figures in Tables II and VII, III and VIII, IV and IX are compared, that the ratios of each pair tend at higher temperatures towards the same limiting value. This is, of course, owing to the fact that at higher temperatures the curvature in each case diminishes, and if these curves become, above  $120^\circ$ , practically horizontal straight lines, the ratios obtained at identical temperatures would become the same as those obtained at corresponding temperatures. This would seem to show that for analogous substances at least a true estimate of the effect of chemical constitution on rotation may be derived by direct comparison of rotations at one temperature provided that the curves in the neighbourhood of that temperature are almost horizontal.

It remains to be seen whether this idea is capable of extension. It will be applied in some other simple cases, and for that purpose data are at present being collected.

#### SUMMARY.

1. It is shown that methyl tartrate is capable of existence in a solid form melting at  $61.5^{\circ}$ .

2. Data for the variation of rotation with change of temperature of methyl, ethyl, and *n*-propyl tartrates are given.

3. It is shown that comparisons of these data at identical temperatures are of little value, especially at low temperatures.

4. Since the rotations of methyl, ethyl, and *n*-propyl tartrates vanish at  $0^{\circ}$ ,  $-34^{\circ}$ , and  $-60^{\circ}$  respectively, it may be assumed that these substances are in corresponding optical conditions at these temperatures, and in general that at  $T^{\circ}$ ,  $(T-34^{\circ})$ , and  $(T-60^{\circ})$  the methyl, ethyl, and *n*-propyl esters will also be in corresponding conditions as regards rotation.

5. It is shown that comparisons effected at corresponding temperatures are much more satisfactory than those obtained at identical temperatures.

6. If the rotations are taken at corresponding temperatures, the increment of  $2\text{CH}_2$  in passing from methyl to ethyl tartrate rather more than doubles the rotation, whilst the next increment of  $2\text{CH}_2$  in passing to *n*-propyl tartrate increases the rotation 1.41 times. The rotation of *n*-propyl tartrate is therefore almost three times that of methyl tartrate.

7. These regularities persist within wide limits of temperature.

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## LXXVIII.—*A Revision of the Atomic Weight of Rubidium.*

By EBENEZER HENRY ARCHIBALD.

THE results obtained from the investigation of the atomic weight of caesium (Richards and Archibald, *Proc. Amer. Acad. Arts and Sciences*, 1903, 38, 443) seemed to show that the analysis of the chloride, bromide and nitrate of this element could be carried out with considerable accuracy. It was thought that the methods elaborated for the analysis of the caesium salts could be applied

with almost equal advantage to the case of the salts of rubidium. If then pure rubidium compounds could be prepared, it would be desirable to subject the atomic weight of this element to the same rigorous test which had been applied in the case of caesium.

*Review of Earlier Investigations.*

Bunsen, who first determined the atomic weight of rubidium (*Poggendorff's Ann.*, 1861, 113, 339), estimated the amount of silver chloride precipitated by a weighed amount of rubidium chloride, and his weighings, when corrected for air displacement, gave the following values for the atomic weight of rubidium: 85·36, 85·36, 85·59, 85·28, giving a mean value of 85·40, these being calculated on the basis of  $O = 16$ , with  $Cl = 35·455$  and  $Ag = 107·93$ .

To remove traces of potassium, Bunsen precipitated his rubidium several times as the platinichloride. Whilst this treatment would eventually remove the potassium, it would nevertheless require a very large number of precipitations.

The next observer to study the atomic weight of rubidium was Piccard (*J. pr. Chem.*, 1862, 86, 454; *Zeit. anal. Chem.*, 1862, 1, 519), who used the same methods of purification and analysis as those employed by Bunsen, but appears to have subjected his rubidium carbonate to many more fractionations with alcohol in order to get rid of any trace of caesium; this treatment would tend to raise the percentage of potassium present, whereas, as already indicated, the previous precipitations as the platinichloride would hardly be sufficient to remove the last traces of this metal.

Moreover, in correcting the observed weights of silver chloride, this experimenter assumed that the portion of the precipitate finally adhering to the filter was entirely reduced to silver during ignition, and as total reduction is highly improbable this assumption may have vitiated the results to an appreciable extent. The results of Piccard's four determinations gave a mean value of 85·44 ( $O = 16·0$ , &c.).

In 1876, Godeffroy (*Ann. Chim. Pharm.*, 1876, 181, 185) published the results of four determinations of the chlorine in rubidium chloride, the method of analysis being practically the same as that used by the earlier investigators. His method of purifying the rubidium material was based on the work of Redenbacher (*Sitzungsber. Wiener Acad.*, 1865, 51, 247), who pointed out the difference in solubility of the alums of rubidium and caesium, and showed how this fact might be made use of in separating these elements. As the caesium alum is the less soluble, the impossibility of getting rid of the last trace of caesium from a sample of rubidium alum by recrystallisation is apparent; and this might account for the higher values obtained

by this observer. His analysis gave the mean value of 85.50 ( $O = 16.0$ ). The results of a number of analyses of rubidium chloride and bromide were published by Heycock (*British Association Report*, 1882, 499), but as the details regarding his experiments were not given, one cannot form an opinion as to their accuracy. He found the ratio of silver to rubidium chloride and of silver to rubidium bromide. The mean of seven analyses of the chloride gave the ratio  $Ag : RbCl :: 107.93 : 120.801$ , indicating an atomic weight for rubidium of 85.344. From the analysis of the bromide, the ratio found was  $Ag : RbBr :: 107.93 : 165.390$ , or an atomic weight of 85.389.

If an average is taken of the mean results calculated from the data given by the earlier investigators, the value 85.42 is obtained.

### *The Analysis of Rubidium Chloride.*

In preparing a pure salt of rubidium from material which contains traces of both potassium and caesium, one must keep in view the relation of rubidium to these two elements. As regards the properties of its compounds, it stands midway between potassium and caesium, and any treatment which will lower the proportion of one in the material may tend to increase the percentage of the other. For example, when the last traces of potassium have been removed from a rubidium compound by recrystallisation, the rubidium compound being more insoluble than the corresponding compound of potassium, then if any caesium was originally present, the final portion of rubidium salt will contain a much higher percentage of this impurity. It is also evident that a rubidium compound free from caesium cannot be prepared by taking a middle portion from which several fractions of crystals have been deposited, as the mother liquor from these crystals will always contain a quantity of caesium, depending on the solubility of the caesium salt in this medium. It will therefore be necessary to convert this salt into that of another acid, the rubidium salt of which is less soluble than the caesium; recrystallisation of this compound will then give a rubidium compound practically free from caesium.

This principle was kept in view in the preparation of the pure rubidium salts. The material used was rubidium iodide obtained from two sources, one specimen coming from Haen, of List, Germany, the other from Eimer and Amend, of New York. Whatever be their origin, these samples differed to a considerable extent as regards purity; the former containing a large percentage of potassium and traces of caesium, whilst the latter was spectroscopically free from both these metals.

It was thought that the best method of removing the potassium from the rubidium material would be by recrystallising one of the trihalide salts. This method has been suggested and used by Wells

(*Amer. J. Sci.*, 1901, [iii], 43, 17; *Chem. News*, 1901, 84, 2184), and was found to give very pure material in the case of caesium. As the rubidium dichloriodide is nearly ten times less soluble than the corresponding potassium compound, and crystallises quite readily on cooling a saturated solution, this salt was first tried. About 150 grams of the German sample of rubidium iodide was converted into the dichloriodide and subjected to many fractional crystallisations. An approximately equal amount of the New York sample, which showed in the spectroscope no indication of the presence of potassium or caesium, was also converted into this salt, and likewise recrystallised. After each crop of crystals had been separated from their mother liquor, they were carefully drained and washed with a little aqua regia. The iodine, a little of which had to be added during these fractionations, had been carefully resublimed.

When ten crystallisations had been made of the first portion of salt, 35 grams were set aside for treatment which would remove the caesium present. It was noted that after five crystallisations the potassium line could not be found in the spectrum of the salt when a good single prism spectroscope was employed, and hence the five subsequent fractionations should give a salt practically free from this impurity; nevertheless, after the 35 grams had been removed, the remainder was thrice recrystallised, and the product converted into another salt in order to remove the caesium.

As another test for the presence of potassium, the mother liquors from the last four fractionations of the dichloriodide were combined, the trihalide salt converted into the normal chloride, and fractionated by precipitating with hydrochloric acid, but no potassium could be detected in the final precipitate.

The second 150 grams of rubidium iodide were treated like the first sample, except that, as the salt was purer at the beginning, only eight crystallisations were made before a portion was set aside, and the remainder received three additional crystallisations. The portion which had been fractionated eleven times gave a very faint caesium line when tested in the spectroscope, whereas the caesium lines could not be found in the original salt or even in the sample which had been fractionated eight times.

It will be seen that four different samples of rubidium dichloriodide have thus been obtained. If the potassium has not been entirely removed from the portion which has received the least number of recrystallisations, it will be present in different proportions in all four samples, and therefore, if all are treated in the same manner when removing the caesium, four different values for the atomic weight of rubidium should be obtained on analysis, the first portion giving the lowest value and the last the highest.

The removal of the caesium was the next point to be considered. Whereas the methods used by Bunsen and Godeffroy for separating rubidium and caesium can be employed with advantage in preparing pure caesium material, they are not suitable for removing the last traces of caesium from a rubidium salt; Johnson and Allen (*Amer. J. Sci. and Arts*, 1863, [ii], 35, 94), however, have shown that rubidium hydrogen tartrate is about eight times less soluble than the caesium salt, and fractional recrystallisation of this salt should therefore remove all traces of caesium.

It was also thought advisable to see whether the caesium could not be removed by precipitating the chlorides with hydrochloric acid. As the rubidium chloride is much less soluble in hydrochloric acid than the caesium chloride, this might prove a simple and convenient method of removing this impurity. For this purpose, the two portions of dichloriodide first prepared, which had been recrystallised eleven and eight times respectively, were converted into the normal chloride by heating in a porcelain basin in an electric drying oven at a temperature of  $75^{\circ}$  until all the iodine and excess of chlorine had been expelled. These preparations were then dissolved separately in platinum basins in the least amount of hot water, and precipitated with hydrogen chloride, generated by boiling a moderately concentrated hydrochloric acid solution. The salt which separated was washed on a platinum Gooch crucible with a little hydrochloric acid, redissolved in water, and again precipitated. This process of precipitation was repeated ten and fifteen times respectively for the above samples of salt; the portion which, as the dichloriodide, had been recrystallised eight times was now reprecipitated fifteen times, whilst the portion which had received eleven recrystallisations as the trihalide salt was reprecipitated ten times with hydrogen chloride. These two fractions of rubidium chloride will be referred to as samples I and II. It is evident that from the treatment sample I has received, both as the trihalide salt and also when precipitated as the chloride, it should contain the higher percentage of potassium; whilst according to the same reasoning a greater percentage of caesium should be found in sample II.

The tendency for the formation of the platinichloride when the chloride is in contact with platinum in the presence of an excess of hydrochloric acid is not so marked here as in the case of caesium; nevertheless, the temperature was not allowed to rise above  $60^{\circ}$  or  $70^{\circ}$  when precipitating with hydrogen chloride.

The two other portions of rubidium dichloriodide referred to above were treated differently for the removal of the caesium present. After converting them into the normal chloride in the same manner as before, each portion was dissolved in water and evaporated with pure redistilled sulphuric acid. Barium hydroxide, which had been repeatedly crystal-

lised, was then added to the solution of rubidium sulphate, until only a trace of sulphuric acid remained. After the barium sulphate, tartaric acid was added in double the quantity necessary to neutralise the rubidium hydroxide, when crystals of the hydrogen tartrate at once separated. The tartaric acid employed, which had been crystallised several times, was perfectly free from ammonia, and left no residue on ignition.

The portion of the hydrogen tartrate which had separated was now fractionally crystallised five times, then converted into the chloride, precipitated twice with hydrogen chloride, and set aside for analysis. This fraction will be referred to as sample III. The second portion of the hydrogen tartrate, which received eight fractional crystallisations, was then converted into the chloride and precipitated with hydrogen chloride. This treatment furnished sample IV.

While these fractionations for the removal of the caesium were being carried out, portions were tested from time to time by means of the spectroscope to ascertain whether the treatment was having the desired effect. In the case of samples I and II it was found that after four precipitations as the chloride the caesium lines had entirely disappeared from the spectrum, although they were quite distinct when the original sample of chloride was tested. After two crystallisations as the hydrogen tartrate, the caesium lines were no longer present in the spectrum of portions of sample IV, but in this case the percentage of caesium present in the original salt was much smaller.

The last three mother liquors from each of all these samples were evaporated to dryness, the residues converted into the dichloriodide, and repeatedly fractionated by recrystallising, until a very small quantity remained. Portions from each of these four end-products, when examined in the spectroscope, did not exhibit any caesium.

It would seem that a few more fractionations—perhaps in the ratio of three to two—are required when the caesium is being removed from the rubidium compound by precipitating the chloride with hydrogen chloride, than when the separation is effected by recrystallising the hydrogen tartrate, but the ease with which the former process can be carried out will often render it preferable, whilst there is much less likelihood of introducing impurity.

Shortly, we have now four samples of rubidium chloride to be analysed. The first two, prepared from the German salt, have been crystallised ten and fifteen times as the dichloriodide, and fifteen and ten times respectively as the chloride. The last two preparations, from the salt obtained in New York, have been crystallised eight and eleven times as the dichloriodide, and eight and five times respectively as the hydrogen tartrate.

The method of preparing the silver was practically the same as that

pursued by Richards and Parker (*Proc. Amer. Acad.*, 1896, 32, 55) in their investigation on the atomic weight of magnesium. After precipitating the silver as chloride, the precipitate was thoroughly washed with several litres of distilled water, treated for several days with aqua regia, and then reduced with a solution of invert sugar and sodium hydroxide. After thorough washing, the reduced silver was redissolved in nitric acid, reprecipitated, and washed as before, and then, having been reduced from the chloride and again washed, fused on sugar charcoal before the blow-pipe. A portion of this fused silver was now dissolved in nitric acid, the excess of acid removed, the silver nitrate dissolved in water, and the solution diluted until it contained about twenty per cent. of silver. The greater part of the silver was deposited electrolytically from this solution, using a very weak current, when silver crystals of considerable size were obtained. The anode was wrapped in filter paper to prevent the anode dust from contaminating the rest of the solution.

The silver crystals were now removed from the solution, thoroughly washed, and fused in a boat made by igniting a mixture of pure lime and anhydrous calcium nitrate. The fused silver was cut into pieces of the proper weight with a clean steel chisel, and these, after successive treatment with hydrochloric acid, ammonium hydroxide, and nitric acid, were kept under distilled water.

The acids used were carefully redistilled, rejecting the first and last portions of the distillate; the nitric acid was always tested in the nephelometer for the presence of chlorine ions (Richards, *Proc. Amer. Acad.*, 1894, 30, 385).

The water used in this research, which had been redistilled and condensed in block tin vessels, had a very low electrical conductivity, and showed no evidence of the presence of ammonium compounds or chlorides.

#### *Method of Analysis.*

It has been shown by Richards (*Proc. Amer. Phil. Soc.*, 1903, 42, 28, 42, 172) that the fusion of such a salt as rubidium chloride is necessary before one can be certain that the last traces of moisture have been expelled. It has also been shown by Johnson and Allen (*loc. cit.*) that fusion of caesium or rubidium chloride in a moist atmosphere was likely to cause decomposition; as in their analysis of caesium chloride, where the fusion took place in the air of the laboratory, a solution of the fused salt was always found to be slightly alkaline. In the present instance, the fusion of the substance was effected in an atmosphere of pure dry nitrogen, the product being subsequently bottled in an atmosphere of dry air. To secure the first conditions, air was forced through a strong solution of ammonia, then over heated copper, and the

resulting nitrogen passed successively through dilute sulphuric acid, two wash-bottles containing strong sulphuric acid, an eprouvette containing caustic potash, a tube packed with freshly sublimed phosphoric oxide, and a combustion tube where the fusion and subsequent bottling took place. A detailed account of this bottling apparatus will be found in Richards and Parker's paper already cited, and the following figure will give an idea of its construction.

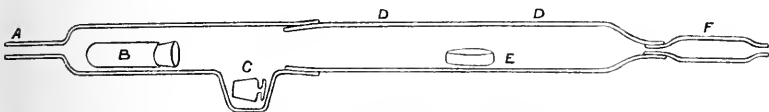


FIG. 1.—*Bottling Apparatus, Horizontal Section.*

*A* = tube leading from phosphoric pentoxide; *B* = weighing bottle; *DD* = hard glass tube; *E* = platinum boat containing fused rubidium chloride; *F* = tube containing phosphoric oxide to prevent any moist air from diffusing inward.

By means of a Y-tube, a stream of dry air can, at any time, be substituted for the nitrogen. A platinum boat of known weight was placed in a weighing bottle provided with a tightly-fitting glass stopper. Another weighing bottle was prepared having the same weight as the first and containing a quantity of platinum equal in weight to the platinum boat. After prolonged desiccation, the platinum boat and its bottle were carefully weighed, using the other bottle and its platinum as a counterpoise. A few grams of the rubidium chloride were weighed into the platinum boat, the boat then placed in the combustion tube, the weighing bottle pushed into position, and the tubes connected.

A current of dry nitrogen was now passed through the apparatus for about half an hour in order to sweep out any moist air, and while this stream of gas was still passing, the salt was gradually heated until it melted. After it had been fused for a few minutes, it was allowed to cool slowly, and the apparatus then swept out with a stream of dry air. When the air had completely displaced the nitrogen, the boat was pushed into its bottle, the stopper pushed home, and the bottle and contents transferred to the desiccator.

The bottles were left in the desiccator for perhaps two hours; a careful weighing was then made before the salt was dissolved in about two-thirds of a litre of water contained in an Erlenmeyer flask, fitted with a ground glass stopper. These solutions were always found to be neutral and quite free from any insoluble residue. The platinum boat lost only 0.3 milligram after about twenty determinations, and never showed any sign of having been acted on by the fused salt.

A quantity of silver, slightly in excess of the amount necessary to precipitate the chlorine in the rubidium chloride taken, was now weighed out and dissolved in nitric acid. Every precaution was taken, while the metal was dissolving, to prevent any of the silver being carried away with the escaping vapours. After the metal had dissolved, the solution was diluted to about 500 c.c. The silver nitrate was slowly added to the solution of rubidium chloride in a dark room. The contents of the flask were now vigorously shaken for half an hour, in order to coagulate the precipitate and shake out any occluded silver nitrate, the mixture being then left in the dark for several hours.

A Gooch crucible fitted with a mat of carefully selected asbestos, which had been thoroughly purified by treatment with acids, was dried in an electric oven for an hour at  $125^{\circ}$  and then tared against another platinum crucible having approximately the same weight.

The mother liquor from the precipitated silver chloride was filtered through the crucible and the precipitate washed twice by shaking it vigorously each time with about 150 c.c. of water, these washings being then added to the main filtrate. An additional 300 c.c. of water were shaken up with the precipitate, and after several hours poured through the filter, this filtrate being kept separate. This treatment was repeated with about the same amount of water, and the silver chloride then washed on to the filter, dried for several hours at  $125^{\circ}$ , desiccated for two or three hours, and then weighed.

The foregoing operations were carried out in either a very subdued or a ruby-red light; the precipitate was also protected from the light while drying and was never exposed to strongly actinic rays.

The amount of silver chloride which had been dissolved by the 600 c.c. of washing water was estimated by the method worked out by Richards (*loc. cit.*). By means of a nephelometer, a solution containing a known amount of silver was compared with the unknown solution, hydrochloric acid being added to the former and silver nitrate to the latter. The amount of silver chloride found in the washing water was of course added to the observed weight of the precipitate.

The asbestos carried away in the filtrate was estimated when necessary by filtering the solution through an ashless filter and weighing the residue after ignition; it never amounted to more than 0.25 milligram.

The amount of moisture still remaining in the dried pellet of silver chloride was estimated by Stas's method, namely, by heating the precipitate just to fusion in a tared porcelain crucible, the loss being then subtracted from the observed weight of silver chloride.

Before the ratio of silver to rubidium chloride could be determined, it was necessary to know the excess of silver in the filtrate from the

silver chloride precipitate. This was estimated by adding hydrochloric acid in slight excess to the filtrate, washing and weighing the precipitated silver chloride in the manner previously indicated. In this case, a little hydrochloric acid in the washing water prevented any appreciable amount of the silver chloride from dissolving.

In order to correct the observed weights of rubidium chloride for the buoyancy of the atmosphere, it was necessary to know the specific gravity of this salt. For this purpose, pure dry redistilled toluene was employed (b. p.  $110^{\circ}$ ), since rubidium chloride was found to be quite insoluble in this liquid. The specific gravity of the toluene at  $20^{\circ}$  referred to water at  $4^{\circ}$  was found to be 0.8650, whilst Richards found the value 0.8646 (*Proc. Amer. Acad.*, 1895, 31, 158).

1.1170	fused RbCl displaced	0.3511	toluene at $20^{\circ}$ .	Sp. gr. = 2.752.
1.8080	"	"	0.5678	" 20°. Sp. gr. = 2.755.

The mean specific gravity of the rubidium chloride is therefore 2.753, this being a little lower than the value 2.807 given by Setterberg (*Oefvers. Stockh. Acad. Forh.*, 1882, 39, 23).

The specific gravity of silver chloride has been carefully determined by several observers; for the purpose of this research it was taken to be 5.55.

The long-armed Troemner balance, which was employed in this work, was sensitive to 0.02 milligram with a load of forty grams, and had an aluminium beam, the rest of the metal being gold-plated. The weights were carefully compared among themselves, according to the method suggested by Richards (*J. Amer. Chem. Soc.*, 1900, 22, 144).

During the course of the investigation on the atomic weight of caesium (*loc. cit.*), several analyses were made of a sample of very pure potassium chloride in order to test the method and also the purity of the silver used. This precaution was taken in the present case with equally satisfactory results. The value found for the atomic weight of potassium agreed closely with the number given in the former paper, which in turn was in accord with the value found by Stas. The results do not appear here, as the observations are being extended, and will form the subject of a future communication.

### *Results of the Analysis of Rubidium Chloride.*

The ratios of silver chloride to rubidium chloride obtained from the analysis of the four samples of material are shown in Table I. In computing these values, and any others given below, the atomic weights of silver, chlorine, and bromine were taken to be 107.93, 35.455, and 79.955 respectively; oxygen being 16.000.

TABLE I.

No. of analysis.	Sample of RbCl.	Weight of RbCl <i>in vacuo.</i>	Weight of AgCl <i>in vacuo.</i>	Ratio AgCl : RbCl = 100·000 : <i>x</i> .	Atomic weight of rubidium.
1	I	1·99966	2·37070	84·349	85·489
2	I	2·06480	2·44778	84·354	85·496
3	I	2·29368	2·71960	84·339	85·475
				Average (a)...	85·487
4	II	1·09495	1·29796	84·360	85·502
5	II	2·14381	2·54118	84·364	85·507
6	II	2·89700	3·43475	84·344	85·482
				Average (b)...	85·497
7	III	2·19692	2·60452	84·350	85·491
8	III	2·14543	2·54386	84·338	85·473
9	III	2·12164	2·51557	84·341	85·477
10	III	2·25777	2·67685	84·344	85·482
				Average (c)...	85·481
11	IV	2·18057	2·58528	84·346	85·484
12	IV	2·32699	2·75878	84·348	85·488
13	IV	4·00035	4·74233	84·354	85·495
14	IV	2·43440	2·88613	84·348	85·488
				Average (d)...	85·488

The following table contains the ratios of silver to rubidium chloride.

TABLE II.

No. of analysis.	Sample of RbCl.	Weight of RbCl <i>in vacuo.</i>	Weight of silver <i>in vacuo.</i>	Ratio Ag : RbCl = 100·000 : <i>x</i> .	Atomic weight of rubidium.
15	I	1·99966	1·78454	112·054	85·485
16	I	2·06480	1·84241	112·070	85·503
17	I	2·29368	2·04710	112·046	85·478
				Average (e)...	85·488
18	II	1·09495	0·97702	112·070	85·503
19	II	2·14381	1·91316	112·056	85·488
20	II	2·89700	2·58550	112·047	85·479
				Average (f)...	85·490
21	III	2·19692	1·96076	112·044	85·475
22	III	2·14543	1·91462	112·055	85·486
23	III	2·12164	1·89346	112·052	85·483
24	III	2·25777	2·01515	112·040	85·471
				Average (g)...	85·479
25	IV	2·18057	1·94594	112·057	85·489
26	IV	2·32699	2·07668	112·053	85·484
27	IV	4·00035	3·56998	112·055	85·486
28	IV	2·43440	2·17233	112·064	85·496
				Average (h)...	85·488

In the foregoing experiments, 28·69865 grams of silver yielded 38·12529 grams of silver chloride, giving the ratio

$$\text{AgCl} : \text{Ag} = 100\cdot000 : 75\cdot274.$$

The ratio found by Stas was 75·276. This agreement serves to show the purity of the silver used, and also indicates that the amount of occlusion of alkali chloride or silver nitrate by the precipitated silver chloride must have been inappreciable.

From the above average values it will be seen that the different samples of salt have given the following results :

Sample I	mean of (a) and (e)	85·487
Sample II	„ „ (b) „ (f)	85·494
Sample III	„ „ (c) „ (g)	85·480
Sample IV	„ „ (d) „ (h)	85·488

The varied treatment to which the different samples have been subjected does not seem to have altered them as regards their purity, and one is therefore justified in assuming that the potassium or caesium has been practically all removed, even from that sample which received the least number of crystallisations. Further treatment of the chloride or additional analysis of this salt would seem at present to be of little use.

#### *The Analysis of Rubidium Bromide.*

It now appeared desirable to obtain another ratio from which to calculate the atomic weight of rubidium, as this would necessitate a certain amount of variation in the experimental conditions of the analysis, and thereby render it possible to eliminate any constant error which might be present in the analysis of the chloride.

A number of analyses of rubidium bromide were accordingly carried out by precipitating the bromine as silver bromide and estimating the amount of silver necessary for complete precipitation, as well as the amount of silver bromide produced. The bromine used in preparing the rubidium bromide and hydrobromic acid was purified by dissolving in calcium bromide and reprecipitating by adding a large volume of water. The bromine was then redistilled six times, the first and last portions of the distillate being rejected in each operation. The hydrobromic acid was prepared from the rectified bromine and thoroughly washed red phosphorus. It was washed, collected, and redistilled five times, the first and last portions of the distillate being discarded in each case.

The rubidium material for the bromide determinations, which consisted of the residues from the previous analyses together with a

portion of sample IV, was converted into the hydrogen tartrate, and after three crystallisations had been made of this salt, one portion was analysed, whilst the remainder received two more fractionations. These two portions were converted successively into the bromide and tribromide, and the latter thrice crystallised in order to remove any sodium or potassium which might have found its way into the material during these operations; as in the case of the chloride, the final mother liquors, both from the hydrogen tartrate and tribromide fractionations, were examined in the spectroscope for the presence of caesium or potassium, but there was no indication of the presence of either of these metals. The normal bromide was now prepared from the trihalide salts by gently heating in an electric oven, dissolved in a little hot water, twice precipitated with hydrobromic acid, and dried. The two samples will be referred to as I and II. The method of analysis was essentially the same as in the case of the chloride, with this exception, that dry hydrogen bromide was mixed with the nitrogen which passed through the apparatus while the bromide was being fused. The solutions of the fused salt were always found to be neutral and the platinum boat was not attacked.

In each case, the amount of silver necessary to precipitate the bromine from the portion of salt taken was estimated by precipitating the excess with hydrobromic acid, filtering, and weighing in the manner already described in the case of the chloride. The correction for the solubility of the silver bromide in water was of course much smaller than that for the chloride.

In order to reduce the weighings of rubidium bromide to the vacuum standard, the following specific gravity determinations were made. The bromide was found to be insoluble in pure toluene, which, as before, had a sp. gr. 0.865 at 20°.

1.2401 fused RbBr displaced	0.3271 toluene at 20°.	Sp. gr. = 3.279
0.9795    "       "       "	0.2580       "       "   20°.	Sp. gr. = 3.284

---

Mean..... 3.282

This mean result is appreciably smaller than the value 3.358 found by Setterberg (*loc. cit.*).

The results of the analysis of the two samples of rubidium bromide given on p. 789 are expressed in the units already employed in the case of the chloride.

From these results, we see that 13.97953 grams of silver produced 24.33539 grams of silver bromide; therefore the bromide must have contained 57.445 per cent. of silver. This is identical with the

TABLE III.

*Ratios of Silver Bromide to Rubidium Bromide.*

No. of analysis.	Sample of RbBr.	Weight of AgBr <i>in vacuo.</i>	Weight of RbBr <i>in vacuo.</i>	Ratio AgBr : RbBr = 100·000 : $x$ .	Atomic weight of rubidium.
29	I	3·04578	2·68170	88·047	85·471
30	I	2·35401	2·07280	88·054	85·486
31	I	2·38589	2·10086	88·053	85·485
				Average (i)...	85·480
32	II	2·96462	2·61044	88·053	85·484
33	II	4·36215	3·84082	88·049	85·475
34	II	4·29084	3·77852	88·061	85·499
35	II	4·93210	4·34299	88·056	85·488
				Average (j)...	85·486

TABLE IV.

*Ratios of Silver to Rubidium Bromide.*

No. of analysis.	Sample of RbBr.	Weight of Ag <i>in vacuo.</i>	Weight of RbBr <i>in vacuo.</i>	Ratio Ag : RbBr = 100·000 : $x$ .	Atomic weight of rubidium.
36	I	1·74930	2·68170	153·301	85·502
37	I	1·35230	2·07280	153·280	85·479
38	I	1·37061	2·10086	153·278	85·478
				Average (k)...	85·486
39	II	1·70300	2·61044	153·285	85·486
40	II	2·50590	3·84082	153·272	85·471
41	II	2·46502	3·77852	153·287	85·488
42	II	2·83340	4·34299	153·278	85·477
				Average (l)...	85·480

value found by Stas. Bringing together these average values, we obtain a mean value, thus:

Average (i).....	85·480
„ (j).....	85·486
„ (k).....	85·486
„ (l).....	85·481

Mean value..... 85·483

The mean value of the chloride determinations = 85·487

The final mean value = 85·48 gram being gram), it was

It seems most unlikely that, after such varied treatment, an appreciable quantity of potassium or caesium can be present in all these samples in the same proportion, or in such proportion as to give identically equivalent weights for the rubidium. If an appreciable amount of caesium still remains in this material, there is not much hope of its being removed by any known method of separation.

The lower value obtained by former investigators must have been due chiefly to the presence of potassium in their material. This metal is almost as difficult to remove as the caesium, whilst its detection by means of the spectroscope gives a great deal more trouble. In fact, the amount of either caesium or potassium which may be present in the rubidium material before its presence can be detected by a good prism spectroscope is much larger than is generally supposed, so effectually are the lines masked by the bright rubidium spectrum.

The foregoing results seem to show that the atomic weight of rubidium cannot be far from 85.48. It is hoped that a study of the decomposition of rubidium nitrate in the presence of silica will be taken up before long and made the subject of a future communication.

In conclusion, I wish to thank Dr. B. J. Harrington, director of the chemistry building, for his kindness in placing valuable apparatus and material at my disposal.

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MONTREAL.

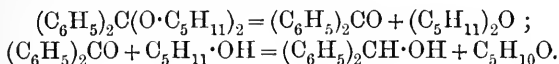
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## LXXIX.—*The Action of Sodium Methoxide and its Homologues on Benzophenone Chloride and Benzylidene Chloride. Part II.*

By JOHN EDWIN MACKENZIE and ALFRED FRANCIS JOSEPH.

In a previous paper on this subject, one of us described the preparation of dipropoxy- and diisobutyloxy-diphenylmethanes and dihydroxy-tetraphenylmethane as well as the products obtained by the action of certain sodium alkyl oxides on benzylidene chloride. The research has been extended to the naphthols, and some experiments with aliphatic alcohols have been repeated.

By the action of sodium *iso*amyloxyde on benzophenone chloride, a minute quantity of crystals melting at 66—67° had been obtained, the constitution of which could not then be explained, but on repeating the experiment larger amounts have been separated, and the crystals have been proved to be benzhydrol. The formation of benzhydrol may be explained by supposing that di*iso*amyloxydiphenylmethane is first decomposed into benzophenone and *iso*amyl ether, the former being then reduced by the *iso*amyl alcohol present :



This substance is also formed in the preparation of di*isobutyloxy*- and di*isopropyloxy*-diphenylmethanes. It is curious that this reaction should take place only in the case of secondary alcohols.

Satisfactory products have not yet been obtained as a result of the action of  $\alpha$ -naphthol on benzylidene chloride, but from  $\beta$ -naphthol a substance has been isolated which is identical with that produced by Claisen (*Annalen*, 1887, 237, 261) on condensing  $\beta$ -naphthol with benzaldehyde in the presence of hydrochloric acid under increased pressure, or of acetic and sulphuric acids under the atmospheric pressure. The reaction may be supposed to take place according to the equation :



A study of the interactions of the naphthols and benzophenone chloride is being carried on by Mr. Albert Shrimpton.

## EXPERIMENTAL.

### *Benzhydrol.*

In attempting to prepare di*iso*amyloxydiphenylmethane, 4·6 grams of sodium dissolved in 80·5 grams of amyl alcohol (b. p. 131—131·5°) were heated at 150° for 14 hours with 23·7 grams of benzophenone chloride, and as the product was still alkaline, 2·3 grams of benzophenone chloride were then added and the heating continued for another 10 hours. Ether was added to the cold product in order to precipitate the sodium chloride, and, after evaporating the ether, the excess of amyl alcohol was distilled off under reduced pressure. The residue, when placed in a mixture of ice and salt, became semi-solid and remained so at the ordinary temperature, but melted at a slightly higher temperature. An analysis of this product indicated that it is a mixture of amyl alcohol with di*iso*amyloxydiphenylmethane.

As the product still contained sodium chloride (0·0153 gram being found in the platinum boat after the combustion of 0·71 gram), it was

extracted with dry ether, the solution filtered and evaporated, and the residue cooled in a freezing mixture. In this way, crystals were separated which melted at 65—66°, the melting point not altering when the substance was mixed with benzhydrol prepared by other methods. On combustion, the following figures were obtained :

0.3376 gave 1.0473 CO<sub>2</sub> and 0.2082 H<sub>2</sub>O. C = 84.60 ; H = 6.85.

C<sub>13</sub>H<sub>12</sub>O requires C = 84.78 ; H = 6.52 per cent.

The following cryoscopic determinations were made by Mr. G. W. Clough :

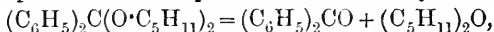
0.0402 in 16.448 benzene gave  $\Delta t = 0.079^\circ$ . M. W. = 154.7.

0.0968 „ 16.448 „ „  $\Delta t = 0.185^\circ$ . M. W. = 159.0.

C<sub>13</sub>H<sub>12</sub>O requires M. W. = 184.0.

To prove the absence of optical activity, polarimetric readings were taken of a 5 per cent. solution in benzene, but no rotation was observed in a polarimeter reading to 0.01°.

As a further proof that the substance was benzhydrol, some crystals were kept over sulphuric acid in a vacuum desiccator for twelve days, at the end of which time the loss in weight only amounted to 1 per cent. Had the substance been the diisoamyl compound, it should have become decomposed into benzophenone and diisoamyl ether,



in accordance with the behaviour of its homologues.

In the former description of the preparation of diisobutyloxydiphenylmethane (Trans., 1901, 79, 1207), it will be noticed that a very small amount of crystalline substance melting at 62—64° and generally agreeing in properties with benzhydrol was obtained. The analytical numbers (C = 84.53 ; H = 6.86 per cent.) showed it to have a composition agreeing closely with that of benzhydrol.

### *Dibenzoyldiphenylmethane.*

To the description of this substance formerly given (Trans., 1896, 69, 992) may be added the fact that, like its homologues, it may be decomposed into benzophenone and dibenzyl ether. On heating in a dry test-tube at 220° for half an hour, a colourless liquid condensed on the upper part of the tube, and the residual oil solidified on cooling. The solid distilled between 250° and 300° under atmospheric pressure, and the colourless crystals which separated in the distillate, after drying on a porous plate, melted at 48—49° and showed the characteristic properties of benzophenone.

*The Anhydride of Phenyl-di- $\beta$ -hydroxynaphthylmethane.*

Benzylidene chloride (14.7 grams) was mixed with a large excess of  $\beta$ -naphthol (52 grams) in a round-bottomed flask and heated at  $100^{\circ}$ , at which temperature a copious evolution of hydrogen chloride took place. As the reaction subsided, the temperature was raised to  $120^{\circ}$  and kept there for eight hours, at the end of which time no further evolution of gas took place. The loss in weight amounted to 7.3 grams, the theoretical loss calculated for  $2\text{HCl}$  being 6.6 and that for  $2\text{HCl} + \text{H}_2\text{O}$  being 8.3. In another experiment, the actual loss was 8.3 grams, the calculated numbers being 7.3 and 9 respectively. The violet residue was powdered and extracted with carbon disulphide, in which it readily dissolved. From the solution, a colourless, crystalline powder was precipitated by the addition of a large volume of alcohol, the yield amounting to 73 per cent. of the calculated amount. This powder was found to be sparingly soluble in cold alcohol, ether, or acetic acid, easily so in chloroform or carbon disulphide, and moderately so in hot acetic acid. By recrystallisation from the last-named solvent, colourless, glistening leaflets were obtained, melting at  $190\text{--}191^{\circ}$  (Claisen gives  $189\text{--}190^{\circ}$ ). A specimen which had been kept in a vacuum desiccator over soda-lime was employed in the following analysis:

0.1632 gave 0.5397  $\text{CO}_2$  and 0.07887  $\text{H}_2\text{O}$ .  $\text{C} = 90.19$ ;  $\text{H} = 5.37$ .

$\text{C}_{27}\text{H}_{18}\text{O}$  requires  $\text{C} = 90.50$ ;  $\text{H} = 5.03$  per cent.

Attempts to determine the molecular weight by the cryoscopic method were unsuccessful owing to the slight solubility of the substance. The following results were obtained by the ebullioscopic method, using chloroform as solvent:

0.2034 in 21.24 chloroform gave  $\Delta t\ 0.108^{\circ}$ .  $\text{M. W.} = 325$ .

$\text{C}_{27}\text{H}_{18}\text{O}$  requires  $\text{M. W.} = 358$ .

This substance does not yield  $\beta$ -naphthol on fusion with caustic potash.

Other modifications of the method of preparation have been tried, but with less favourable results. On gradually adding a xylene solution of benzylidene chloride to a boiling solution of  $\beta$ -naphthol in the same solvent, a steady evolution of hydrogen chloride takes place, but the product is decolorised with great difficulty.

In the hope of obtaining phenyl-di- $\beta$ -hydroxynaphthylmethane,  $\text{C}_{27}\text{H}_{20}\text{O}_2$ , itself, experiments were made with sodium naphthoxide and benzylidene chloride, but only the anhydride,  $\text{C}_{27}\text{H}_{18}\text{O}$ , could be isolated. An alcoholic solution of 15.7 grams of  $\beta$ -naphthol was added to

a solution of 2.5 grams of sodium in the same solvent, and the alcohol removed by heating first in a water-bath and then in an air-bath, a current of dry air being passed over the residue, which was then mixed with 8.7 grams of benzylidene chloride and the mixture heated at 130° for 15 hours. No hydrogen chloride was evolved, and the solid mixture was extracted with carbon disulphide, leaving a residue of sodium chloride which weighed 6.5 grams, the calculated amount being 6.3 grams. The solution, when concentrated and treated with alcohol, gave a sandy, crystalline precipitate. When crystallised from glacial acetic acid, the crystals melted at 191° and agreed in all their properties with the foregoing anhydride.

Qualitative experiments with acetylated naphthols and benzylidene chloride yielded negative results.

#### *Nitration of the Anhydride.*

Although the experimental conditions were varied, pure compounds could not be isolated, the analytical numbers indicating that di-, tri-, penta-, and hexa-nitro-compounds had been formed.

A mixture of 20 grams of fuming nitric acid (sp. gr. 1.5) and 100 grams of glacial acetic acid was added to 5 grams of the anhydride suspended in 50 grams of glacial acetic acid, the whole being well cooled. A yellow powder and a deep orange solution resulted, the former being collected, then washed with boiling glacial acetic acid and dried in a vacuum desiccator over solid caustic soda. This substance melted with decomposition at 252—253° and was analysed with the following result, which indicated a dinitro-derivative :

0.4074 gave 23.3 c.c. moist nitrogen at 20° and 766 mm.  $N = 6.59$ .

$C_{27}H_{16}O(NO_2)_2$  requires  $N = 6.25$  per cent.

In another experiment, 1.8 grams of the anhydride mixed with 20 c.c. of nitric acid (sp. gr. 1.4) were heated in a water-bath for 3 hours, a red solution being produced, from which a yellow powder separated on cooling. The filtrate from this powder was poured into a large volume of water, and the yellow precipitate thus obtained was heated with glacial acetic acid, in which it only partially dissolved. The portion insoluble in acetic acid charred at about 250° and gave the numbers recorded in analysis I.

The solution in acetic acid on dilution with water yielded a precipitate, the analysis (II) of which showed it to consist mainly of the trinitro-compound.

I. 0.16069 gave 9.6 c.c. moist nitrogen at 16.2° and 762 mm.

$N = 7.0$ .

II. 0.13122 gave 10.3 c.c. moist nitrogen at 13° and 744 mm.  
N = 9.03.

$C_{27}H_{16}O(NO_2)_2$  requires N = 6.25 per cent.

$C_{27}H_{15}O(NO_2)_3$  „ N = 8.52 „

In a third experiment, the anhydride (3.5 grams) was added to 40 c.c. of nitric acid (sp. gr. 1.5) cooled in ice; it dissolved with effervescence, and after half an hour the mixture was poured on to crushed ice. The yellow precipitate (I) thus obtained was dissolved in glacial acetic acid, and on cooling a yellowish-red powder separated which charred at about 200°. Fractional precipitation of the acetic acid solution by the addition of water gave several precipitates, the last of which was analysed (II).

I. 0.1118 gave 11.7 c.c. moist nitrogen at 14.2° and 752 mm.  
N = 12.17.

II. 0.1633 gave 18.75 c.c. moist nitrogen at 15.5° and 760 mm.  
N = 13.5.

$C_{27}H_{13}O(NO_2)_5$  requires N = 12.0 per cent.

$C_{27}H_{12}O(NO_2)_6$  „ N = 13.38 „

#### *Action of Sulphuric Acid on the Anhydride.*

According to Trzcinski (*Ber.*, 1883, 16, 2839, and 1884, 17, 500), an acid, which he calls “melinoin-trisulphonic acid,” is obtained by the action of concentrated sulphuric acid on benzaldehyde and  $\beta$ -naphthol. In our experiments, the only product obtained was a  $\beta$ -naphthol-disulphonic acid, which was isolated in the form of its barium salt.

Five grams of the powdered anhydride were mixed with 20 c.c. of fuming sulphuric acid and left for a week, after which the mixture was poured on to ice; the product, which dissolved completely, was neutralised with barium carbonate, and on concentrating the clear solution, crystals were obtained, which, when recrystallised from hot water, yielded colourless needles (1.8 grams). Analysis of these crystals (I) showed them to be a barium  $\beta$ -naphtholdisulphonate containing six molecules of water of crystallisation. By evaporating the mother liquors, 3.6 grams of a red, glassy substance (II) were obtained having approximately the same composition:

I. 0.6408 at 105° lost 0.1216.  $H_2O = 18.98$ .

II. 0.7526 „ 105° „ 0.1404.  $H_2O = 18.68$ .

I. 0.4225 salt dried at 105° gave 0.212  $BaSO_4$ . Ba = 29.27.

II. 0.5347 salt not dried at 105° gave 0.235  $BaSO_4$ . Ba = 25.86.

I. 0.452 salt dried at 105° gave 0.4532  $CO_2$  and 0.0902  $H_2O$ .

C = 27.34; H = 2.2.

$C_{10}H_6O_7S_2Ba \cdot 6H_2O$  requires  $H_2O = 19.72$ ; Ba = 25.05 per cent.

$C_{10}H_6O_7S_2Ba$  requires C = 27.4. H = 1.38; Ba = 31.26 „

These results show that the anhydride has undergone decomposition.

When warmed in the water-bath for some hours with concentrated sulphuric acid (sp. gr. 1.84), the anhydride gives a red solution, which, when poured on to ice, slowly deposits an orange-red powder, leaving a bright red liquid. The colour is removed from both powder and liquid by the addition of caustic alkalis, and is restored by acids.

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### LXXX.—*The Formation of Periodides in Nitrobenzene Solution. Part II. Periodides of the Alkali and Alkaline Earth Metals.*

By HARRY MEDFORTH DAWSON and ETHEL ELIZABETH GOODSON, B.Sc.

PREVIOUS experiments on the nature of nitrobenzene solutions containing iodine and potassium iodide (Dawson and Gawler, Trans., 1902, 81, 524) have now been extended to iodides of the other alkali metals, to ammonium and substituted ammonium iodides, including phenyl-, phenyldimethyl-, and tetramethyl-ammonium iodides, and to the iodides of the alkaline earth metals. These experiments consist in measuring both the solubility of the various iodides in nitrobenzene containing dissolved iodine and also the solubility of iodine in nitrobenzene containing one or other of the foregoing iodides. The iodides, with the exception of lithium iodide, are not appreciably soluble in nitrobenzene, but dissolve readily in the presence of iodine; similarly, iodine only dissolves to the extent of 0.2 gram-molecule per litre in pure nitrobenzene, whereas its solubility is much greater in presence of the iodides. These facts are of essential importance in drawing conclusions from the experimental data.

The object of the present investigation being to ascertain and compare the general behaviour of the various iodides towards iodine rather than to determine with the greatest possible accuracy the quantitative relationships in any particular case, it was considered sufficient, as the result of some preliminary experiments, to carry out the solubility measurements at the ordinary temperature. In a few cases, *o*-nitrotoluene was used as solvent instead of nitrobenzene, previous experiments (Dawson, Trans., 1904, 85, 467) having shown that in the case of potassium iodide these behave very similarly in regard to the formation of periodides.

In the analysis of the solutions, the iodine was determined by titration with sodium thiosulphate, and, in order to obtain the concentration

of the iodide, a measured volume of the solution was in most cases subjected to distillation in steam, the last traces of the solvent being removed by extraction with carbon disulphide and subsequent repeated evaporation to dryness on the water-bath. The residue was then heated for some time at  $130^{\circ}$ , and finally over the free flame. In some cases, this mode of procedure could not be adopted, but reference will be subsequently made to special methods.

*Solutions Saturated with Iodide.*

The following table contains the experimental data for solutions containing iodine and saturated with regard to the iodide indicated. The iodine and iodide concentrations are given in grams and gram-molecules per litre, and in the last column the ratio of iodine to iodide molecules is represented.

TABLE I.  
Sodium iodide.

Iodine concentration		Iodide concentration		Mol. ratio, I <sub>2</sub> /Iodide.
In grams.	In gram-mols.	In grams.	In gram-mols.	
33.0	0.130	19.9	0.133	0.98
60.6	0.239	34.9	0.233	1.03
107.5	0.424	53.9	0.360	1.18
173.5	0.684	78.7	0.525	1.30
332	1.31	118	0.787	1.66
479	1.89	152	1.015	1.86
735	2.90	197	1.315	2.21
959	3.78	218	1.455	2.60

Rubidium iodide.

98.1	0.387	75.8	0.357	1.08
269	1.06	171	0.806	1.31
421	1.66	237.5	1.12	1.48
606	2.39	295	1.39	1.72

Cesium iodide (in *o*-nitrotoluene).

47.3	0.186	46.4	0.178	1.04
96.1	0.379	86.5	0.333	1.14
155.2	0.612	129	0.496	1.24
158	0.622	127.6	0.491	1.26

TABLE I (*continued*).

## Lithium iodide.

Iodine concentration		Iodide concentration		Mol. ratio, $I_2/\text{iodide}$ .
In grams.	In gram-mols.	In grams.	In gram-mols.	
160	0.640	146	1.09	0.58
216	0.853	175.5	1.31	0.65

## Tetramethylammonium iodide.

48.0	0.189	38.6	0.192	0.99
88.3	0.348	70.3	0.350	1.00
142.5	0.562	108	0.537	1.05

## Strontium iodide.

72.0	0.284	47.7	0.122	2.3
------	-------	------	-------	-----

## Barium iodide.

66.0	0.260	35.1	0.90	2.9
186	0.735	89.9	0.23	3.2

In the case of the lithium solutions, the concentration of the iodide was determined by distilling in steam, and, after removing the nitrobenzene by extraction with carbon disulphide and subsequent evaporation, by precipitating the aqueous solution with silver. The strontium and barium solutions were treated in a similar manner and the metals precipitated as sulphates. In the case of ammonium iodide, the measured volume of solution was first shaken up with sufficient sodium thiosulphate solution to react with all the periodide iodine; the mixture was then made alkaline, and the ammonia estimated by distillation in steam and absorption in standard acid.

An inspection of the experimental data recorded in the previous table shows that the behaviour of the various iodides subjected to investigation is in general very similar to that previously observed in the case of potassium iodide. For small iodine concentrations (0.2 gram-molecules per litre), the molecular ratio of dissolved iodine to iodide is approximately equal to unity, the inference being that triiodides of the type  $MI_3$  are, under these conditions, the essential components of the solutions. This holds, at any rate, for the more completely investigated potassium, sodium, rubidium, caesium, and tetramethylammonium iodide solutions. As the iodine concentration increases, the molecular ratio  $I_2/\text{iodide}$  also increases, and this in all

probability corresponds with the formation in solution of periodides of gradually increasing complexity. In the case of sodium iodide, where the range of concentration investigated is greatest, the molecular ratio  $I_2/NaI$  increases from unity at the smallest concentrations to 2.6 at a concentration of 960 grams of iodine per litre.

All the iodides investigated, with the exception of lithium iodide, exhibit similar relationships, but considerable differences are evident when a quantitative comparison is made. If the iodine concentrations are plotted as abscissæ and the values of the molecular ratio  $I_2/\text{iodide}$  as ordinates, the curves obtained for the different iodides are by no means coincident. The curve for sodium iodide lies above that for the potassium salt and this lies above the rubidium iodide curve. At a concentration of 2 gram-molecules of iodine per litre, the values of the molecular ratio are respectively 1.90, 1.75, and 1.60. The different values thus obtained for the molecular ratio are probably caused by differences in stability of the corresponding periodides of the various metals. Whether the curves become coincident at low concentrations and run approximately parallel to the abscissa corresponding with  $I_2/\text{iodide} = 1$ , or whether, as seems more likely, the corresponding tri-iodides undergo considerable dissociation with increasing dilution, cannot be decided on the basis of the present experiments. To establish this point it would be necessary to carry out further experiments at small concentrations using larger volumes of solvent. The values of the molecular ratio for strontium and barium iodides are, roughly, twice as large as those obtained for the iodides of the univalent radicles at corresponding concentrations; this difference evidently corresponds with the presence of two iodine atoms in the molecule of the alkaline earth iodides.

Some other points in connection with this series of experiments also require notice. In the investigation of caesium iodide, using *o*-nitrotoluene as solvent, it was found impossible to prepare solutions saturated with caesium iodide containing more than about 0.5 gram-molecule of iodide per litre (Expts. 3 and 4). The addition of iodine in quantities corresponding with much larger concentrations always leads to a solution, the composition of which is represented by the numbers of Expts. 3 and 4. The iodine is evidently used up in the formation of caesium tri-iodide, which is present as a solid phase, the solution of maximum concentration being thus in equilibrium with caesium tri-iodide and caesium iodide. In accord with this view, it was found that on decanting off the solution obtained by agitating for several hours 10 c.c. of *o*-nitrotoluene with 4 grams of iodine and 6 grams of caesium iodide, and on shaking the residue with a further 10 c.c. of the solvent until equilibrium had been attained, the second solution had the same composition as the original one. The molecular

concentration of iodine in this limiting solution is greater than that of caesium iodide; it seems probable, therefore, that the periodide is partially decomposed in contact with the solvent, caesium iodide separating, and excess of iodine passing into solution. With nitrobenzene as solvent, more concentrated caesium iodide solutions can be obtained than with *o*-nitrotoluene.

The abnormal behaviour of lithium iodide, which is clearly shown in the small value of the molecular ratio  $I_2/LiI$ , is due to the fact that the iodide itself dissolves to a considerable extent both in nitrobenzene and in *o*-nitrotoluene. On shaking lithium iodide with either of these solvents, it is rapidly changed and light yellow, crystalline plates are formed of considerably smaller specific gravity than the original iodide, which subside very slowly. Analysis of the solutions obtained by agitating the iodide with nitrobenzene and *o*-nitrotoluene for about 12 hours gave respectively 51 and 30 grams of lithium iodide per litre. These numbers are only to be regarded as approximate, for the solutions were yellow in colour and contained small quantities of free iodine. The observations are, however, quite sufficient to account for the abnormal behaviour of lithium iodide as compared with that of the other iodides examined.

To prepare the yellow, crystalline compound, lithium iodide carefully dehydrated by heating in a current of hydrogen was agitated with nitrobenzene in a closed vessel at about  $60^\circ$ , the solution being then filtered and allowed to remain in the cold. The crystals, which were freed as far as possible from mother liquor by filtering and pressing on porous plate, are very hygroscopic, and in contact with water immediately decompose into lithium iodide and nitrobenzene. According to the analysis of the crude material thus obtained, the substance has the formula  $LiI, C_6H_5 \cdot NO_2$ , and the compound of the iodide with *o*-nitrotoluene has a similar composition.

#### *Solutions Saturated with Iodine.*

In the second series of experiments, the composition of solutions saturated with iodine and containing one or other of the iodides in the following table was investigated. The arrangement of the experimental data is exactly the same as in the previous table.

TABLE II.

Iodine concentration		Iodide concentration		Mol. ratio, I <sub>2</sub> /Iodide.
In grams.	In gram-mols. per litre.	In grams.	In gram-mols. per litre.	
Sodium iodide.				
125	0.492	13.55	0.0905	5.4
204	0.804	27.7	0.185	4.35
246	0.969	35.0	0.234	4.1
393	1.55	57.7	0.385	4.0
532	2.09	79.8	0.533	3.9
738	2.91	109.1	0.728	4.0
954	3.76	142	0.948	4.0
1170	4.60	186	1.24	3.7
1251	4.93	228	1.52	3.3
Rubidium iodide.				
421	1.66	85.4	0.402	4.1
761	3.00	158	0.745	4.0
1060	4.18	217.5	1.025	4.1
Caesium iodide (in <i>o</i> -nitrotoluene).				
213	0.840	48.2	0.186	4.5
364	1.435	89.7	0.345	4.1
637	2.51	164.3	0.632	4.0
858	3.38	223	0.858	3.95
Lithium iodide (in nitrobenzene).				
642	2.53	84.1	0.628	4.0
Ammonium iodide (in nitrobenzene).				
482	1.90	69.5	0.480	4.0
Ammonium iodide (in <i>o</i> -nitrotoluene).				
669	2.64	94.3	0.651	4.0
Aniline hydriodide.				
721	2.84	164	0.74	3.9

TABLE II (*continued*).

Iodine concentration		Iodide concentration		Mol. ratio, I <sub>2</sub> /Iodide.
In grams.	In gram-mols. per litre.	In grams.	In gram-mols. per litre.	
Dimethylaniline hydriodide.				
626	2.47	160	0.64	3.9
Tetramethylammonium iodide.				
266	1.05	49.3	0.245	4.3
280	1.10	51.4	0.256	4.3
Strontium iodide.				
599	2.36	106.5	0.312	7.6
Barium iodide.				
237	0.934	42.2	0.108	8.6
345	1.36	68.7	0.176	7.7
455	1.715	84.8	0.217	7.9
809	3.19	158.5	0.405	7.9

The analysis of the various solutions was carried out by the methods already described, except in the case of aniline and dimethylaniline hydriodides. For the purpose of the present investigation, it was considered sufficient to estimate the iodide concentration in these two cases by comparison with corresponding solutions of the other iodides. The increase in volume of the solvent in the formation of solutions of aniline and dimethylaniline hydriodides containing quantities of iodine represented by the experimental data in the above table has been assumed to be the same as in the formation of solutions containing the same quantity of iodine and one of the easily estimated metallic iodides. By carrying out the solubility experiments with a weighed quantity of each of the two iodides and a measured volume of the solvent, the concentration of the substituted ammonium iodides in the resulting solution could be thus determined comparatively with sufficient accuracy.

According to the data in the table, the solubility of iodine in nitrobenzene is very largely increased by the presence of iodides of the alkali and alkaline earth metals and of ammonium and substituted ammonium iodides, and this increased solubility is most simply explained by the assumption of the formation of complex periodides in

the solution. In general, four molecules of iodine pass into solution for each molecule of dissolved alkali, ammonium, or substituted ammonium iodide, whilst eight molecules dissolve for each molecule of the dissolved iodide of an alkaline earth metal.

A few points regarding the individual iodides may be mentioned before considering further the general nature of these experimental results. As in the first series, the solubility measurements have been made over a considerably greater range of concentrations in the case of sodium iodide than in that of the other iodides. As previously observed for potassium iodide solutions (*loc. cit.*), the molecular ratio  $I_2/NaI$  is considerably greater than 4 when the amount of dissolved iodide is small, but this is undoubtedly due to the simple solubility of iodine in the solvent independently of the formation of soluble periodides. According to Expts. 8 and 9, the molecular ratio, after remaining constant over a considerable range of concentration, diminishes at very large concentrations, and although the cause of this has not been determined with certainty, yet there is some evidence to show that under these conditions the solution is approximating to a condition of saturation with regard to two components.

In the case of tetramethylammonium iodide, the quantities of iodine and iodide employed in each of the two experiments were both in excess of the amounts found in the resulting solutions. The two solutions are practically identical, and the observations indicate that a solution of this composition is in equilibrium with two solid phases, one of which is iodine and the other a tetramethylammonium periodide. By reference to Table I, it will be seen that, with excess of iodide, solutions containing much larger quantities of tetramethylammonium iodide than the solution in Table II can be obtained. The solution being thus in equilibrium with two solid phases, the molecular ratio  $I_2/\text{iodide}$  has not the same significance as in the case of the other iodides, although its value does not differ much from the value obtained from the remaining iodides at a corresponding concentration.

In general, the relationships evidenced by the solubility data in Table II are in accord with the conclusion that complex periodides of the type  $M'I_9$  are the essential components of the solutions saturated with iodine. These enneaiodides are formed not only by the alkali metals, but also by the ammonium and substituted ammonium radicles. In a similar manner, it may be inferred that, in the case of the alkaline earth metals, strontium and barium periodides of the type  $M''I_8$  are formed, and these may also be referred to as enneaiodides. In both series, each iodine atom in the simple iodide combines with eight other atoms of iodine, and the formation of these enneaiodides appears to be essentially independent of the positive radicle. The fact that the solutions of these periodides are good conductors of

electricity is evidence of their electrolytic dissociation, and it is probable that complex iodine anions represented by  $\overline{I_9}$  are present in the various solutions. It is proposed to examine the electrochemical properties of these solutions more closely.

The conclusion that enneaiodides of the alkali and alkaline earth metals exist in solution receives perhaps some support from the fact that such enneaiodides of substituted ammonium and diammonium radicles have been obtained as solid, crystalline substances. Tetramethyl- and trimethylethyl-ammonium enneaiodides were obtained by Geuther (*Annalen*, 1887, 240, 66) by dissolving the calculated quantities of the simple iodide and iodine in warm alcohol previously saturated with iodine in the cold and allowing to cool. In a paper published since the completion of our experiments, Strömholm (*J. pr. Chem.*, 1903, 67, 345) describes crystalline enneaiodides derived from phenyltrimethyl-, phenyldimethylethyl-, and possibly triethylmethyl-ammonium iodides. The method used by this investigator consists in shaking the simple iodide (or the corresponding tri- or penta-iodide) with a saturated ethereal solution of iodine, repeating the operation with fresh quantities of solution so long as iodine is taken up by the solid substance. Several of the less complex (tri- and penta-) periodides used in these experiments have been previously described by Weltzien (*Annalen*, 1854, 91, 33; 1856, 99, 1) and by Müller (*Annalen*, 1858, 108, 1), and several hepta-iodides were obtained by Geuther (*loc. cit.*). By the same method, Strömholm prepared the enneaiodide of the bivalent radicle trimethylenehexamethyldiammonium, corresponding with the formula  $CH_2(CH_2 \cdot NMe_3 I_9)_2$ . Of eight such tetra-substituted ammonium iodides, five, or possibly six, were found to yield enneaiodides by treatment according to the foregoing method. In no case were periodides higher than the enneaiodide obtained, and, as Strömholm points out, it seems probable that the enneaiodide represents the highest limiting type of periodide.

This view is in agreement with the results of our experiments on the composition of solutions containing iodides of the alkali and alkaline earth metals when saturated with iodine. In these experiments, with the conditions favourable to the formation of the highest type of periodide, the data obtained indicate the formation of soluble enneaiodides. In respect of their capacity to yield periodides, the alkali and alkaline earth metals are therefore to be placed in the same class as the substituted ammonium derivatives, for some of which the limiting enneaiodides have been isolated.

It is perhaps not unnecessary to point out that the experiments in this paper have reference solely to the nature of the periodides in solution, and are not concerned with their possible existence in the

free state. The substances separating from solution are by no means necessarily identical with the chief components of the solution, and it is therefore noteworthy that the investigation of the products of crystallisation and of the soluble components both lead to the result that the highest periodides of the substituted ammonium radicles are the enneaiodides. In regard to the question of the dependence of the affinity of the iodide for the periodide iodine on the nature of the positive radicle, our experiments give no information.

No special attempts have been made during the course of the investigation to isolate the periodides present in the various solutions. In some few cases the more concentrated solutions were cooled to  $-20^{\circ}$ , with the object of promoting crystallisation, but without success. The two most concentrated solutions obtained in the experiments on the solubility of sodium iodide (Table I, Expts. 7 and 8), however, slowly deposited crystals, which were separated and pressed on porous plate. The crystals from the two solutions gave almost identical results on analysis, the mean percentages being  $I = 53.9$ ,  $NaI = 16.9$ , and  $C_6H_5 \cdot NO_2$  (by difference)  $= 29.2$ . The mother liquors, on the other hand, differed considerably in composition, the values of the molecular ratio,  $I_2/NaI$ , being respectively 2.2 and 2.6. The substance thus obtained is probably a compound of sodium penta iodide and nitrobenzene, represented by the formula  $NaI_5 \cdot 2C_6H_5 \cdot NO_2$ , which requires  $I = 56.0$ ,  $NaI = 16.6$ , and  $C_6H_5 \cdot NO_2 = 27.4$  per cent. For a crude product thus obtained, the agreement between the numbers is sufficiently good. The crystals have a green metallic appearance and deliquesce in the air; benzene, carbon disulphide, or carbon tetrachloride extracts iodine and nitrobenzene, leaving sodium iodide.

To ascertain whether the iodides of the other metals of the first and second groups of the periodic table, namely, copper, silver, and gold, or zinc, cadmium, and mercury, are capable of forming soluble periodides under the same conditions, similar experiments were made with the iodides of silver and cadmium. These were shaken with a nitrobenzene solution of iodine, but the resulting liquids were quite free from iodide, indicating that periodides are not formed in these cases. An attempt to examine the behaviour of hydrogen iodide was foiled by the reducing action of this substance on the solvent leading successively to the production of aniline and aniline hydriodide.

Solutions containing periodides are also obtained when iodine and the bromides of the alkali metals are brought together in the presence of nitrobenzene. Although the nature of these solutions has not been investigated in detail, yet it may be of some interest to record the data obtained in experiments with potassium bromide. The numbers in the following table express the composition of solutions containing

potassium bromide and iodine when saturated with respect to one or other of these substances.

Solutions saturated with potassium bromide.

Iodine concentration, gram-mols.					
per litre .....	0.375	0.758	1.40	2.01	(2.52)
KBr concentration, gram-mols. per					
litre .....	0.157	0.270	0.45	0.61	(0.71)
Mol. ratio $I_2/KBr$ .....	2.4	2.8	3.1	3.3	(3.55)

Solutions saturated with iodine.

Iodine concentration, gram-mols. per					
litre .....	0.765	1.187	1.58		(2.52)
KBr concentration, gram-mols. per litre.	0.169	0.304	0.415		(0.71)
Mol. ratio $I_2/KBr$ .....	4.5	3.9	3.8		(3.55)

To determine the concentration of bromide in the solution, a measured volume was distilled in steam, extracted with carbon disulphide, evaporated to dryness, and the residue weighed, this being afterwards precipitated with silver solution and reweighed as silver salt.

The two series of solutions approximate in composition as the concentration increases, and the identity of the two final solutions indicates that saturation with regard to both components has now been reached. The composition of the solutions saturated with iodine makes it appear probable that the complex perhalogen compounds present in solution are of the same type as those in solutions of the alkali iodides, although the evidence in support of this view is not nearly so decisive.

The chlorides of the alkali metals also form periodides in nitrobenzene solution, although only to a comparatively small extent, for, whereas the chlorides are practically insoluble in pure nitrobenzene, they dissolve to some extent in the presence of iodine. Experiments were made with the chlorides of potassium, rubidium, and caesium, and the solubility of these in nitrobenzene containing 0.2 gram-molecule of iodine per litre was found to be respectively 0.030, 0.044, and 0.080 gram-molecule per litre. These data scarcely admit of comparison with those obtained in the case of the iodides, being of quite a different order of magnitude. The increase in the molecular proportion of dissolved chloride from potassium to caesium is probably to be taken as an indication of the increasing stability in solution of their corresponding perhalogen derivatives. The influence of the

metal as thus indicated agrees with that observed in experiments made with the view of preparing perhalogen derivatives of the alkali metals in the free state.

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### LXXXI.—*Caproylthiocarbimide*.

By AUGUSTUS E. DIXON, M.D.

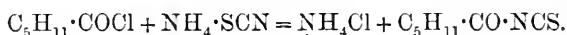
IN previous papers, the author has described the formation of various aliphatic acidic "thiocarbimides" and their combinations with bases, alcohols, &c.; the compounds of this class hitherto obtained include, amongst the purely aliphatic derivatives, propionylthiocarbimide (Trans., 1896, 69, 855), isobutyrylthiocarbimide (*ibid.*), valerylthiocarbimide (*ibid.*, 1895, 67, 1040), and the thiocarbimides of palmitic and stearic acids (*ibid.*, 1896, 69, 1593); to this series, caproylthiocarbimide may now be added.

Reasons have been adduced by the writer (compare Trans., 1901, 79, 542; 1904, 85, 350) and by R. E. Doran (Proc., 1904, 20, 20) for believing that such substances are generally tautomeric in function, behaving either as thiocarbimides or as thiocyanates, or sometimes as both together, according to the conditions imposed; this appears also to be the case for the compound which forms the subject of the present paper, but the account here given of its combinations is limited to a description of experiments conducted with a view to developing its thiocarbimidic power alone, in order to secure data for comparison with the results already obtained for its homologues.

#### *Caproylthiocarbimide*.

To isolate this compound, caproyl chloride, diluted freely with benzene, was mixed with an equal weight of dry, finely powdered ammonium thiocyanate; interaction commenced spontaneously, with the generation of heat, and the clear solution, after a few minutes' boiling, ceased to give the reactions of chlorine. Ammonium chloride and unchanged thiocyanate were filtered off at the pump and the solvent extracted from the filtrate by warming under diminished

pressure; on distilling the residue, practically the whole came over between  $100^{\circ}$  and  $110^{\circ}$ , under 23 mm. pressure, and from this distillate, after two rectifications, a mobile liquid was obtained boiling at  $108^{\circ}$  (uncorr.), under 23 mm. pressure, and amounting to 72 per cent. of that theoretically producible according to the equation:



As freshly distilled, caproylthiocarbimide forms a clear, perfectly colourless, moderately refractive oil having a disagreeable odour, which becomes pungent on heating and excites a flow of tears; it has a sp. gr. = 1.0165 at  $18^{\circ}/15^{\circ}$ . When exposed to the air, it slowly evolves fumes of thiocyanic acid, and, like most other members of the same class, it soon changes on keeping, first assuming a yellow, then a dark red colour, and ultimately becoming turbid.

If thrown into cold water, the oil sinks, rising to the surface if the water is heated, and sinking again as it cools. The rate of attack by cold water is very slow, the aqueous solution obtained by thoroughly shaking the two liquids together giving with ferric chloride only a faint red coloration; such a mixture may be kept for several days without undergoing any considerable change. Hot water decomposes it completely into caproic and thiocyanic acids, but not at all quickly, for prolonged boiling is required before the oily globules disappear; no sign of the evolution of carbon oxysulphide was noticed. On boiling two grams with successive quantities of 15 c.c. of water until dissolved (eight or ten extractions for 15 to 30 seconds each brought the whole into solution), every extract gave an intense red coloration with ferric chloride and a white precipitate with silver nitrate, the precipitate dissolving in ammonia to a nearly clear solution, which darkened only to a very trifling extent on boiling. In relation to water, therefore, the substance behaves essentially as thiocyanate. On the other hand, the original oil, or a drop of the residue left after each of the above operations, produced copious desulphurisation when warmed with ammoniacal silver or alkaline lead solution, the substance under these conditions developing thiocarbimide power to a marked extent. Metallic sulphide, however, is not the sole product of the last-named change, for if the lead mixture is acidified with hydrochloric acid, filtered, and the filtrate treated with ferric chloride, an intense red coloration appears, the material thus manifesting simultaneously the reactions of a thiocarbimide and of a thiocyanate. Analysis was considered unnecessary, having regard to the mode of preparation and general properties of the compound, and to the series of derivatives which it afforded by combination with bases.

*ab*-Caproylphenylthiocarbamide,  $C_5H_{11} \cdot CO \cdot NH \cdot CS \cdot NH \cdot C_6H_5$ .

This substance was prepared by adding a nearly boiling solution of aniline in benzene to a similar solution of pure caproylthiocarbimide; much heat was generated, the mixture boiling freely, and on cooling white crystals soon began to separate. There is no need to use the pure thiocarbimide in this preparation, for its solution, obtained by warming caproyl chloride in benzene with lead or ammonium thiocyanate, may, after filtering, be substituted with advantage. By the latter means, a dirty-brown paste results after the evaporation of the solvent, but from this product, light petroleum extracts a nearly white substance, leaving a small quantity of dark red, viscid oil; the former, when recrystallised from alcohol, came down as a felted mass of slender, white needles, melting at  $77-78^\circ$  without decomposition. The best yield of recrystallised product amounted to 60 per cent. of the theoretical.

Found S = 13.0, N = 11.1;  $C_{13}H_{18}ON_2S$  requires S = 12.80, N = 11.2 per cent.

Caproylphenylthiocarbamide, when heated with water, dissolves slightly, and is deposited again, on cooling, in milky globules which soon crystallise; it is moderately soluble in hot light petroleum or cold alcohol, easily in carbon disulphide or benzene, very freely in ether, chloroform, or hot alcohol. Like many of its congeners of the acidic class, this compound when crystallising entangles a relatively large weight of alcohol, the mixture, as it cools, becoming almost solid; it can be very well crystallised from a mixture of benzene with light petroleum. No trace of red coloration is given by ferric chloride when added to the solution in water or dilute alcohol, or to the mixture produced by boiling the solid with alkali and subsequently acidifying; consequently, the substance is totally devoid of thiocyanic characters. But its cold alcoholic solution gives, with neutral silver nitrate, a white precipitate, rapidly becoming black, and is easily and copiously desulphurised by heating with alkaline lead tartrate. When cautiously warmed with dilute caustic alkali, it dissolves, without melting, to a clear solution; if the latter is now acidified with dilute hydrochloric acid and boiled, caproic acid passes off in the steam, and phenylthiourea gradually separates from the residual liquid; this change occurs as follows:



*ab-Caproyl-o-tolylthiocarbamide*,  $C_5H_{11} \cdot CO \cdot NH \cdot CS \cdot NH \cdot C_6H_4 \cdot CH_3$ .

In making this preparation, instead of the pure thiocarbimide, the solution obtained from caproyl chloride and lead thiocyanate was heated nearly to boiling and added to *o*-toluidine, also dissolved in hot benzene; the mixture boiled violently, and, on concentration, a reddish-yellow, pasty mass was left, from which hot light petroleum extracted an almost white solid; when recrystallised from alcohol, it formed a voluminous mass of long, flexible, white needles, melting without decomposition at  $97-98^\circ$  (uncorr.). In relation to solvents, desulphurising agents, and the action of caustic potash, this substance resembled its lower homologue, and gave, on analysis, 12.3 per cent. of sulphur, against 12.12 calculated for  $C_{14}H_{20}ON_2S$ .

*ab-Caproyl-o-tolylcarbamide*,  $C_5H_{11} \cdot CO \cdot NH \cdot CO \cdot NH \cdot C_6H_4 \cdot CH_3$ .

Silver nitrate was added to an equivalent quantity of the thiocarbamide, both dissolved in hot alcohol; the mixture boiled vigorously, and silver sulphide was precipitated at once; from the filtrate, as it cooled, a nearly white solid crystallised; when recrystallised from light petroleum, microscopic, white needles were obtained, melting between  $99^\circ$  and  $100^\circ$ .

Found  $N = 11.2$ ;  $C_{14}H_{20}O_2N_2$  requires  $N = 11.29$  per cent.

The substance is nearly insoluble in boiling water, very freely soluble in hot alcohol, moderately freely in hot light petroleum, somewhat sparingly so in cold. When heated with dilute caustic alkali, it dissolves to some extent, and the solution, when acidified and boiled, evolves caproic acid; on cooling, a white solid is deposited—probably *o*-tolylurea—but the product was not further examined.

*ab-Caproyl-p-tolylthiocarbamide*,  $C_5H_{11} \cdot CO \cdot NH \cdot CS \cdot NH \cdot C_6H_4 \cdot CH_3$ .

Operating as in the case of the ortho-compound, caproyl-*p*-tolylthiocarbamide was obtained in the form of brilliant, silky, flattened needles, melting at  $90-91^\circ$  (uncorr.) without decomposition.

Found  $S = 12.3$ ;  $C_{14}H_{20}ON_2S$  requires  $S = 12.12$  per cent.

No difference worth recording was found between its general properties and those of its foregoing congeners. By dissolving in warm dilute caustic alkali, the caproyl group is removed, and the solution, when acidified and cooled, deposits crystals of *p*-tolylthiourea.

*ab-Caproyl-p-tolylcarbamide*,  $C_5H_{11} \cdot CO \cdot NH \cdot CO \cdot NH \cdot C_6H_4 \cdot CH_3$ , was

obtained from the preceding compound by treatment with silver nitrate; it is practically insoluble in boiling water, very freely soluble in hot alcohol, rather sparingly so in cold, and crystallises from this solvent in fine, silky needles, melting at  $131-132^{\circ}$  (corr.) and fusing again at the same temperature.

Found  $N = 11.4$ ;  $C_{14}H_{20}O_2N_2$  requires  $N = 11.29$  per cent.

It dissolves, but not very easily, in hot dilute caustic alkali; the solution, when acidified and boiled, evolves caproic acid, and on cooling deposits *p*-tolylcarbamide (m. p.  $173-174^{\circ}$ ).

*Caproylphenylbenzylthiourea*,  $C_5H_{11} \cdot CO \cdot N : C(SH) \cdot N(C_6H_5) \cdot CH_2 \cdot C_6H_5$ .

This was prepared as before, using the pure thiocarbimide and benzylaniline; the yellow paste, left when the solvent had evaporated, on extraction with hot light petroleum, yielded a white, crystalline solid, the weight of which amounted to 89 per cent. of the theoretical. By recrystallisation from hot alcohol, fine, white needles were obtained, melting at  $77-78^{\circ}$  without decomposition; the mother liquor, when allowed to evaporate slowly, gave a further crop of the same substance in large, well-formed, vitreous prisms.

Found  $N = 8.2$ ,  $S = 9.4$ ;  $C_{20}H_{24}ON_2S$  requires  $N = 8.23$ ,  $S = 9.41$  per cent.

The compound is insoluble in water, very freely soluble in hot alcohol, ether, carbon disulphide, benzene, or chloroform; it is miscible with hot light petroleum, although rather sparingly soluble in the cold, and from concentrated solutions is deposited as an oil which rapidly solidifies.

Towards silver nitrate, either neutral or ammoniacal, the substance, for a thiourea, is singularly inert, its alcoholic solution being unaffected even at the boiling point and giving no precipitate; it is only desulphurised imperfectly and with some difficulty by hot alkaline lead tartrate. Its behaviour with caustic potash is peculiar, the solid, when brought into contact with the cold solution, liquefying to a clear oil, but apparently without undergoing any chemical change; if the mixture is boiled and then acidified with hydrochloric acid, the odour of caproic acid becomes distinctly perceptible, but the solution gives no coloration, or practically none, with ferric chloride. If the mixture with caustic potash is thoroughly boiled, cooled, and treated with the lead solution, it remains white; but on heating again, a moderate desulphurisation takes place, originating, no doubt, from the withdrawal of the caproic group, and consequent formation of

*αα*-phenylbenzylthiourea, a substance which is desulphurisable (Trans., 1893, 63, 325) by alkaline lead salts. The easiest way to show the presence of sulphur in this compound is to heat the solid in a dry tube, when it decomposes evolving hydrogen sulphide.

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## LXXXII.—*The Action of Radium Rays on the Halides of the Alkali Metals and Analogous Heat Effects.*

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IN the following experiments, a five-milligram tube of radium bromide was kept in contact with the substances under examination in a dark room, so that the rays had only to pass through the violet glass in order to reach the compound. The results obtained, which present striking analogies to those produced by the action of heat on other substances, relate to the chlorides of the alkali metals (compare *Chem. News*, 1903, 88, 205).

All these substances, except lithium chloride, are coloured by the radium rays; sodium chloride becoming yellow, whilst the corresponding salts of potassium, rubidium, and caesium\* become violet, bluish-green, and green respectively. The amount of absorption of light increases with the atomic weight.

As the colour effects now under consideration cover only a few square millimetres of surface, a special method is required for dealing with them, and an effective criterion for the purpose is presented in the meta-chromatic scale—the sequence of colours obtained by the summation of the effects observed when coloured inorganic substances are heated (compare *Chem. News*, 1893, 67, 27)—this colour scale being as follows: white, violet, blue, green, yellow, orange, red, brown, black.

I have elsewhere entered fully into the construction and uses of this scale (*Chem. News*, 1876, 34, 76 and 77; *Phil. Mag.*, 1876 [v], 2, 423; *Chem. News*, *loc. cit.*), and if it is employed in the present instance to judge the above results it will be seen that the chlorides must be divided into their two sub-groups: I. LiCl, NaCl; II. KCl, RbCl, CsCl.

\* This salt, which had a pale yellow colour, did not give spectroscopic indications of the presence of potassium or rubidium.

*Indications of Molecular Aggregation.*

Constitutive changes brought about by the absorption of external energy are accompanied by changes of molecular aggregation. For the present purpose, the latter may be taken to be indicated by alterations in the quantity  $1/\text{mol. vol.}$  When the temperature of a substance which is changing colour is gradually raised, the value of  $1/\text{mol. vol.}$  decreases. Also in a comparable series of compounds conforming to the constitutive colour law, as we pass in the same order through the meta-chromatic scale,  $1/\text{mol. vol.}$  is a quantity which decreases as the molecular weights increase. The halides under consideration, when viewed from this standpoint, divide themselves into the same sub-groups as are indicated by the colour changes effected by radium rays. These various points are illustrated by the following typical examples :

TABLE I.

*Typical Examples of Compounds conforming to the Constitutive-colour Law\* compared with the Changed Alkali Chlorides.*

Meta-chromatic scale.	The natural colours of comparable series with $1/\text{mol. vol.}$			Halides changed by radium rays with $1/\text{mol. vol.}$	
	An inorganic homologous group.	An isomorphous group.	A vertical group of the periodic classification.	Sub-group I.	Sub-group II.
Black ...	—	—	—	—	—
Brown ...	$\text{K}_2\text{O}(\text{CrO}_3)_3$ 0·006	—	$\text{Cl}_2\text{O}$ 0·060	—	—
Red .....	$\text{K}_2\text{O}(\text{CrO}_3)_2$ 0·009	$\text{Fe}_2\text{O}_3$ 0·0323	—	—	—
Orange ..	—	—	—	$\text{NaCl}$ 0·037	—
Yellow ..	$\text{K}_2\text{O}, \text{CrO}_3$ 0·014	—	$\text{ZnO (hot)}$ 0·068	—	—
Green ...	—	$\text{Cr}_2\text{O}_3$ 0·0325	—	—	$\text{CsCl}$ 0·0236
Blue .....	—	—	—	—	$\text{RbCl}$ 0·0233
Violet ...	—	—	—	—	$\text{KCl}$ 0·025
White ...	—	$\text{Al}_2\text{O}_3$ 0·037	$\text{MgO}$ 0·085	$\text{LiCl}$ 0·041	—

The table shows clearly that the halides of the alkali metals not only form two distinct sub-groups with regard to  $1/\text{mol. vol.}$ , but also

\* The constitutive-colour law may be thus stated :—

In comparable groups of compounds having the general formula  $\text{A}_x\text{B}_y$ , as B increases in weight there is increase of absorption of light in a definite manner, so that the visible effect is a progression in the meta-chromatic scale from the white towards the black end.

that the members of these sub-groups conform to the constitutive-colour law, like the other illustrations given.

*The Evanescence of Colours induced by Radium Rays.*

The colours produced are more or less fleeting, and a comparative study of their evanescence appeared desirable. On bringing the coloured halide out of the dark room, the colour vanished with a speed which varied with the intensity of the daylight. In sunlight, the violet colour of potassium chloride, the pale bluish-green of rubidium chloride, and the green of the caesium salt disappear in less than 30 seconds; in a comparatively dull light, a full minute may be required. The changes follow the indications of the photographer's "actinometer," but are more rapid. Of the other sub-group, only sodium chloride is available; it is comparatively slow, its orange colour taking a couple of hours to disappear in sunlight.

The colour has been observed to be retained in darkness for days in the more sensitive sub-group, whilst sodium chloride in the other series has kept its colour comparatively unchanged for weeks after its production.

In the course of these experiments, the caesium chloride, which was excessively hygroscopic, lost its pale yellow colour on being heated at  $100^{\circ}$  and became white. It appears to exist in two forms, yellow and white, and the latter is turned blue by the radium rays.

*The Relative Expenditure of Energy in Radium Rays effecting Colour Change and a Comparison with Heat Effects.*

In these experiments, the area of surface exposed, the distance traversed by the rays, and the weight of the radium bromide used are constants. It may, moreover, be assumed that the energy emitted per unit of time is also constant. If, therefore, the time be noted which is required to produce a visible effect, the amount of energy expended will be in direct relation to it. Experiments were therefore made to find out the time required to produce a visible colour effect. The radium bromide tube was immersed in the powdered substance to the same extent in every case, and at intervals the salt was brought out of the dark room for momentary examination. The following results were obtained.

TABLE II.

*Colour Changes effected in a Minimum of Time.*

Lithium chloride.	Sodium chloride.	Potassium chloride.	Rubidium chloride.	Cæsium chloride.
No apparent change after several hours.	Change scarcely visible after 30 minutes, but noticeable in 1 hour.	A slight change after 10 minutes ; in 30 minutes, faintly visible.	A faint change in 10 minutes ; plainly visible in 30 minutes.	The change is apparent in 10 minutes and becomes very marked after 30 minutes.

In this case, the yellow cæsium chloride was employed. The results demonstrate that less and less energy is expended in producing colour change as the molecular weight increases, or, in other words, there is an increase in the sensibility to the action of radium rays. A remarkable parallel exists in the case of heat. It follows from Neumann's law that the gram-molecules of each compound in a comparable series require the same amount of heat on being raised from absolute zero to normal temperature ; so that if all were white at absolute zero (a not improbable assumption in the light of recent investigation), then to give them their respective colours at normal temperature equal quantities of heat would have been expended. Now, as the highest members of such a series are most coloured, it follows that in a comparable series of coloured substances there has been most colour change effected with the least expenditure of energy in the members of greatest molecular weight. For example, the oxides of magnesium and zinc are white from  $-273^{\circ}$  to  $0^{\circ}$ . On raising the temperature to  $430^{\circ}$ , the melting point of zinc, the magnesium oxide is still white, but the zinc oxide has become yellow, and there has been approximately the same expenditure of energy in both cases if gram-molecules have been used, but, with equal weights or even equal volumes of the solids, a much smaller expenditure in the case of the zinc oxide, which has double the molecular weight of the magnesia.

*Revivification of the Phosphorescence.*

In comparing the phosphorescence produced by radium rays, it is difficult to get quantitative results under like conditions. Acidity, humidity, state of aggregation, temperature, length of exposure, and eye sensitiveness all more or less affect the data ; nevertheless, an attempt is being made to approximate to comparable conditions.

In the meantime, I have found that within certain limits it is possible to revive the decaying phosphorescence which has been previously excited by the rays from radium bromide. The following details refer to lithium chloride. The salt, when fused in a platinum dish and cooled in a desiccator, had a yellow surface colour, and was not white like the powdered substance. The end of the radium bromide tube was inserted into a slight depression made in the hard surface, and was kept there for 2 days. On removing the tube, a marked localised phosphorescence surrounded by non-phosphorescent surface was observed. Five hours afterwards, when the phosphorescence could no longer be seen, it was brilliantly revived by bringing dark-hot iron near the lithium chloride. Seventeen hours after, this revivification was obtained either by the heat of the hand alone or by raising the temperature to  $37^{\circ}$ . This last experiment was repeated on two successive days, so that on the last occasion revivification was obtained at  $37^{\circ}$  fully 3 days after the original exciting cause had been removed. Other salts in the series were also similarly revived.

It appears to me that in this phenomenon we have the peculiar molecular motion of a radium salt impressed on lithium chloride by means of the radium rays, and having been so impressed this borrowed radium motion can be revived and sustained by invisible heat. This presents a striking analogy to the condition of things which I have suggested as a possible source of the energy of radium (*Chem. News*, 1903, 88, 206).

### *Summary.*

(1) The colour changes produced by radium rays in chlorides of the alkali metals divide these elements into their two sub-groups: I. LiCl, NaCl; II. KCl, RbCl, CsCl; and the changed chlorides conform to the constitutive-colour law.

(2) The division into these sub-groups is also indicated by their differences of molecular aggregation as expressed by the coefficient 1/mol. vol.

(3) There is relative stability of the colours produced while they remain in darkness, and their rate of disappearance or decay in daylight varies with the intensity of the light.

(4) The amount of energy expended by the radium rays in effecting the colour changes decreases as the molecular weight increases, or, in other words, the sensibility to the action of the radium rays increases with the molecular weight.

(5) When the induced phosphorescence has decayed so as to be no longer visible, it can be revived by invisible heat.

(6) In many respects, these phenomena are analogous to the thermal effects produced in other substances, and the whole of the evidence points to the conclusion that they are physical changes.

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### LXXXIII.—*The Viscosity of Liquid Mixtures. Part I.*

By ALBERT ERNEST DUNSTAN, B.Sc.

POISSEULE (*Mem. Inst. Paris*, 1846, 9, 433), who first studied the viscosity of liquid mixtures, found in the case of mixtures of ethyl alcohol and water a well-marked maximum corresponding with the proportions  $3\text{EtOH}, 1\text{H}_2\text{O}$ .

Graham (*Phil. Trans.*, 1861, 151, 373) confirmed Poisseule's work on this mixture, and also investigated a considerable number of others, such as aqueous solutions of the common mineral acids, of acetic and formic acids, and of the common alcohols. He used a constant pressure viscometer, calibrated in terms of water, and in the majority of cases found maximum points corresponding approximately with mixtures of definite molecular composition.

Wijkander (*Weid. Beiblätter.*, 1879, 8, 3) found that at  $20^\circ$  a mixture of the composition  $1\text{MeCO}_2\text{H}, 1\text{H}_2\text{O}$  had a maximum viscosity, but that, as the temperature altered, the maximum point shifted; thus, at  $20^\circ$  it corresponded with 21 per cent. of acetic acid, but at  $50^\circ$  it coincided with 18 per cent. of this acid. He also worked with other mixtures, such as aniline—benzene, ether—carbon disulphide, benzene—ethyl alcohol, ether—chloroform. It will be noticed that most of these liquids are of the non-associated, monomolecular type.

Traube (*Ber.*, 1886, 19, 871) obtained similar results for the alcohol—water mixture, and found that whereas at  $20^\circ$  the maximum was at 44 per cent. alcohol, at  $30^\circ$  it had changed to 46 per cent. ( $1\text{EtOH}, 3\text{H}_2\text{O}$  requires 46 per cent. of alcohol).

Linebarger (*Amer. J. Sci.*, 1896, 2, 331) found that monomolecular liquids, although giving approximately normal results, did not adhere strictly to the law of mixtures, the observed viscosity being always smaller than the calculated value. He worked with mixtures of benzene with ether, toluene, carbon disulphide, carbon tetrachloride, ethyl acetate, chloroform, or nitrobenzene, and of toluene with ethyl benzoate, carbon disulphide, or ether.

In 1897, Thorpe and Rodger published an addendum to their classical paper on viscosity (*Trans.*, 1897, 51, 360) describing the behaviour of a few mixtures of typical monomolecular substances, for example, chloroform, ether, carbon disulphide, and methyl iodide. They found, as Linebarger had done, that in no case could the viscosity of a mixture be accurately calculated from that of its constituents, and in most cases a decrease of viscosity was noticed. In one instance, for benzene—carbon tetrachloride, a difference of 6 per cent. was found between calculated and observed results; moreover, as the temperature increased, the mixtures of benzene and carbon tetrachloride were found to become still less viscous than would be the case if they behaved in a perfectly normal manner. They suggested that benzene has probably a different molecular complexity at varying temperatures, it having been previously shown by them that the viscosity of benzene is considerably greater than that of its homologues. With methyl iodide—carbon disulphide, they obtained a curve having an inversion point, the viscosity being at first greater than that calculated and subsequently less, a fact which would bring this mixture into line with ethyl alcohol—water as an extreme case (see below).

Varenne and Godefroy (*Compt. rend.*, 1903, 137, 993) worked with mixtures of ethyl alcohol and water more fully than hitherto, and, using a constant pressure viscometer of new pattern, obtained a series of discontinuities at the following points :

1EtOH, 3H<sub>2</sub>O; 1EtOH, 2H<sub>2</sub>O; 1EtOH, 6H<sub>2</sub>O; 3EtOH, 2H<sub>2</sub>O; and 1EtOH, 22H<sub>2</sub>O.

Lastly, Wagner (*Zeit. physikal. Chem.*, 1903, 46, 867) quotes several cases of the occurrence of maximum and minimum points; cyanobenzene diminishes the viscosity of ethyl alcohol, nitrobenzene that of *isobutyl* alcohol. *o*-Nitrotoluene in ethyl alcohol gives an inversion point; *m*-nitrotoluene furnishes a minimum and *p*-nitrotoluene a maximum. He suggests that the solute diminishes the concentration of the solvent, causing a lowering of viscosity, but that this diminution may be counteracted by the added viscosity of the solute.

#### EXPERIMENTAL.

The apparatus employed was modelled on that recommended by Ostwald (*Physico-Chemical Measurements*, 1894 ed., p. 163). The viscometer consists of a U-tube, one limb being capillary (15 × 0.05 cm.), terminating at its upper end in a cylindrical bulb of 5 c.c. capacity, with index marks etched above and below it. At the lower end of the other limb is a receiving bulb.

A carefully-measured amount of the liquid is placed in the receiving bulb by a pipette. The liquid, when sucked up above the upper mark,

flows through the capillary by the pressure due to its density, the time of flow for water being 265 seconds. The viscometer is placed in a bath, kept at  $25^{\circ}$  by a thermostat, and stirred by bubbles of carbon dioxide from a Kipp's apparatus. For small baths, this method of stirring is cheap and very efficient. Care must be taken that the maximum variation of temperature is not greater than  $0.1^{\circ}$ ; very considerable errors are otherwise introduced, especially for the more expansible liquids. The observations were usually made in the evenings, so that the bath had had several hours in which to attain to a perfectly steady state.

The instrument was calibrated by using Thorpe and Rodger's results for water at  $25^{\circ}$ ; the calibration has been frequently repeated, but no change has been noticed.

The mixtures were made up from pure chemicals obtained from Kahlbaum, which, in each case, have been redistilled; the components were weighed out to the milligram.

Times of flow were measured by a stop watch (0.2 second), and specific gravities at  $25^{\circ}$ , referred to water at  $4^{\circ}$ , were taken in an Ostwald-Sprengel tube of 2 c.c. capacity.

Every care has been taken to render the conditions uniform throughout the investigation.

### I. *Mixtures containing Non-associated Monomolecular Liquids.*

The preceding references to the work of Linebarger, and Thorpe and Rodger show that the behaviour of mixtures of monomolecular liquids is only approximately normal. In the majority of cases, a sagging takes place in the curve, which may be due, as Wagner suggests, to the diminution of the concentration of the more viscous constituent. It would be more likely due to some slight mutual action, because, as is shown in the sequel, the more affinity there is between the components the greater is the divergence from the normal.

The law of mixtures is never accurately obeyed, and divergences from it seem to be more clearly marked out in the case of viscosity than with other properties, such as refractive index. This divergence from calculated results becomes less as temperature rises, as was pointed out by Thorpe and Rodger (*loc. cit.*). This, again, lends support to the idea that the variations are caused by some affinity leading to the formation of loosely aggregated complexes, which would be decomposed with rise of temperature. In the case of the benzene—carbon tetrachloride mixtures, the variation increases with rising temperature; benzene, however, seems to be abnormal in this respect,

for the authors quoted above show that benzene has a higher viscosity than its homologues. Thus, for benzene solutions we may expect, as temperature rises, some dissociation, and hence a less viscosity.

In view of the relatively large amount of work which has been done on this type of liquid, only one pair was investigated, namely, ethyl acetate and benzene, the sp. gr. of these liquids being 0.8931 and 0.8737 respectively.

Percentage of ethyl acetate.	$\eta$ .	Percentage of ethyl acetate.	$\eta$ .
0	0.005822	48.30	0.004803
27.04	0.005181	49.10	0.004782
33.10	0.004990	75.95	0.004446
35.84	0.004990	100	0.004193
43.93	0.004830		

A considerable amount of sagging is noticed in this curve, which is possibly due to a slight change of condition. The maximum difference between the observed and calculated results occurs at the point corresponding approximately with molecular proportions of the components.

## II. *Mixtures containing Associated Liquids.*

### 1. *Sagged Curves Approximately Normal.*

*Ethyl Alcohol and Carbon Disulphide* (sp. gr. 0.7821 and 1.254 respectively).—The curve given by these liquids is very similar to the preceding case, a slight amount of sagging being observed. The maximum divergence between calculated and observed values is 2 per cent., and occurs at 40 per cent. of carbon disulphide at a point which would nearly correspond with  $2\text{EtOH}, 1\text{CS}_2$ . Hence we may assume that very little mutual action has taken place, each liquid preserving its own viscosity throughout.

Percentage of carbon disulphide.	$\eta$ .	Percentage of carbon disulphide.	$\eta$ .
0	0.01113	52.82	0.006659
16.91	0.009448	69.95	0.005669
19.29	0.009535	73.50	0.005466
25.64	0.009065	81.93	0.004926
32.31	0.008407	100	0.003656
39.50	0.007621		

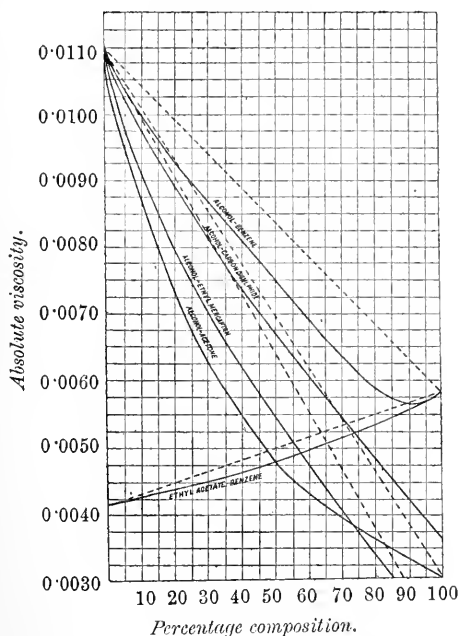
*Mercaptan and Ethyl Alcohol* (sp. gr. 0.8373 and 0.7821 respectively).—A curve precisely similar to the preceding was afforded by these

substances, although there is a considerable amount of sag, a fact which is emphasised in the case of such a pair as acetone—alcohol, in which both liquids are associated.

The maximum sag takes place at 4EtOH,1EtSH. Here more mutual action has obviously ensued. Perhaps mercaptan, having an SH group, may conceivably possess, in a less degree, the properties of a compound containing hydroxyl.

Percentage of mercaptan.	$\eta$ .	Percentage of mercaptan.	$\eta$ .
0	0·01113	32·54	0·006525
3·48	0·01048	35·97	0·006119
9·47	0·009731	44·76	0·005821
12·30	0·009305	68·05	0·004083
13·88	0·008559	100	0·002091
16·25	0·008385		

*Acetone (sp. gr. 0·7900) and Ethyl Alcohol.*—These liquids give a curve which, although rather exaggerated, is like that given by two



monomolecular liquids. Since both these compounds belong to the associated type of substances, a curve such as that given by the alcohol—water mixture, resulting in a well formed maximum, would be

expected. There is, however, a large amount of sagging, the maximum divergence being approximately at the point  $1\text{Me}_2\text{CO}, 1\text{EtOH}$ .

It is worthy of note that mixtures of acetone and water, which are both associated substances, give a maximum in the viscosity curve. There is a very slight indication of a maximum point for the densities of this mixture at molecular proportions.

Percentage of acetone.	$\eta$ .	Percentage of acetone.	$\eta$ .
0	0.01115	43.38	0.005162
22.46	0.007168	44.50	0.005028
27.77	0.006510	51.57	0.004620
35.11	0.005797	70.34	0.003836
36.83	0.005636	100	0.003125

## 2. Mixtures giving Curves with Minimum Points.

*Benzene* (sp. gr. 0.8737) and *Ethyl Alcohol*.—A minimum point is observed in this curve at a concentration of 6 per cent. alcohol, corresponding approximately with  $9\text{C}_6\text{H}_6, 1\text{EtOH}$ . Pickering, when using the freezing point method in his work on the properties of strong solutions, observed a break in the curve with a mixture containing 10.5 mols. of alcohol in 100 mols. of benzene. The rest of the curve approximates to the normal, the viscosity throughout being less than the calculated value. Benzene behaves abnormally in several cases. Thus its coefficient of viscosity is greater than that of toluene, and acids such as acetic tend to form double molecules when dissolved in it.

Wagner (*loc. cit.*) quotes the case of cyanobenzene and nitrobenzene giving diminished values of viscosity when dissolved in ethyl alcohol, so it would appear that this behaviour of benzene is shared by some of its derivatives.

It is certainly a very curious fact that the addition of a much more viscous solute should diminish the viscosity of the solution. The viscosity of alcohol is almost double that of benzene.

Percentage of benzene.	$\eta$ .	Percentage of benzene.	$\eta$ .
0	0.01130	67.58	0.006514
8.47	0.01013	69.49	0.006465
17.00	0.009545	76.53	0.006071
28.90	0.008837	80.38	0.005885
45.60	0.007758	88.03	0.005669
50.91	0.007282	98.86	0.005668
		100	0.005821

*Benzaldehyde* (sp. gr. 1.049—1.050) and *Ethyl Alcohol*.—Very considerable difficulty was experienced in attempting to obtain pure benz-

aldehyde. Its extraordinary instability is shown by the fact that if a mixture of ethyl alcohol and benzaldehyde is kept for a day its viscosity rises to a very great extent. Even during the course of the observations, a noticeable increase of time of flow is apparent. Thus, three successive readings gave times as follows: 6'39''·4, 6'43''·6, 6'45''·0.

The first specimen of benzaldehyde used, which had been kept in the laboratory some months, when redistilled boiled quite steadily, its sp. gr. being 1·050; its viscosity, however, was 0·01445. A regular curve was obtained from its mixture with ethyl alcohol having a minimum point at 31 per cent. benzaldehyde, corresponding with 1PhCHO,5EtOH. A fresh specimen, the density of which was 1·049, only had a viscosity of 0·0132. This gave also a uniform curve, and the same minimum point was obtained. Further experiments are being made with this mixture.

1st Specimen.		2nd Specimen.	
Percentage of benzaldehyde.	$\eta$ .	Percentage of benzaldehyde.	$\eta$ .
0	0·01113	0	0·01113
11·65	0·01092	17·66	0·01052
20·67	0·01050	30·42	0·01031
23·60	0·01051	100	0·01321
32·47	0·01041		
53·96	0·01158		
79·32	0·01308		
90·63	0·01362		
100	0·01445		

### 3. Mixtures of Liquids giving Curves showing Maximum Points.

*Ethyl Alcohol* (sp. gr. 0·7880—0·7896) and *Water*.—Two samples of ethyl alcohol were used for these mixtures, and were obtained from absolute alcohol by distilling over lime and anhydrous copper sulphate.

The water used was carefully purified by repeated distillation over caustic potash and potassium permanganate to free it from traces of grease, which it retains most persistently.

A considerable amount of work has been done on this liquid mixture; the earliest observers (Poissee and Graham) obtained a maximum at 3H<sub>2</sub>O,1EtOH, while Varenne and Godefroy (*loc. cit.*) obtain a series of discontinuities, the chief ones being at 3H<sub>2</sub>O,1EtOH, 2H<sub>2</sub>O,1EtOH, and 6H<sub>2</sub>O,1EtOH, with subsidiary ones at 2H<sub>2</sub>O,3EtOH and 22H<sub>2</sub>O,1EtOH.

There are several noteworthy effects when alcohol and water are mixed; heat is generated, contraction takes place, and the viscosity

risers in quite a remarkable way. At the point  $3\text{H}_2\text{O}, 1\text{EtOH}$ , the viscosity is 0.02368, more than twice that of alcohol and nearly thrice that of water.

From freezing point determinations, Pickering (Trans., 1893, 63, 1072) has shown a break at about 53 per cent. of alcohol, corresponding with  $2\text{H}_2\text{O}, 1\text{EtOH}$ .

Traube (*Ber.*, 1886, 19, 871) pointed out that at  $20^\circ$  the maximum point is at 44 per cent. alcohol, but at  $30^\circ$  it has shifted to 46 per cent.

In the present work, the chief break observed is at  $3\text{H}_2\text{O}, 1\text{EtOH}$ . Subsidiary ones are found at  $2\text{H}_2\text{O}, 1\text{EtOH}$ ,  $4-5\text{H}_2\text{O}, 1\text{EtOH}$ ,  $6\text{H}_2\text{O}, 1\text{EtOH}$ , and an indication of discontinuity with about 3 per cent. alcohol.

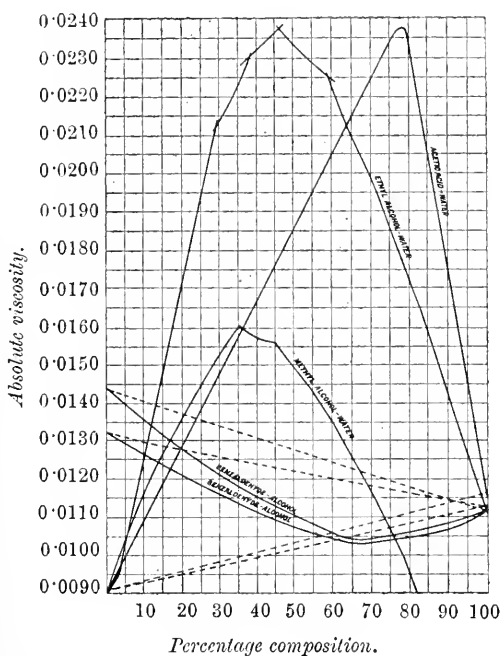
Percentage of alcohol.	$\eta$ .	Percentage of alcohol.	$\eta$ .
0	0.008910	55.58	0.02273
3.60	0.009596	55.83	0.02273
5.09	0.01013	57.51	0.02247
12.50	0.01356	60.15	0.02243
16.00	0.01552	60.17	0.02240
24.66	0.01851	60.49	0.02226
29.63	0.02129	61.06	0.02212
32.40	0.02162	65.36	0.02104
37.39	0.02290	65.85	0.02112
38.26	0.02301	70.54	0.01995
41.21	0.02327	73.90	0.01957
46.17	0.02368	80.20	0.01744
47.72	0.02354	100	{ 0.01113 }
50.20	0.02337		{ 0.01115 }

*Methyl Alcohol (sp. gr. 0.7936) and Water.*—Results were obtained from this mixture very analogous to those from ethyl alcohol—water. Again there was a sudden rise of viscosity with increasing concentration of either constituent. Maxima were obtained at concentrations with 64 per cent. and 54 per cent. of water corresponding with  $3\text{H}_2\text{O}, 1\text{MeOH}$  and  $2\text{H}_2\text{O}, 1\text{MeOH}$ , and there is a very peculiar crater-like depression on the curve between these points. There can be no doubt but that the same cause is in operation here as in the preceding case.

We have, as before, a mixture of substances containing hydroxyl, and, moreover, there is a distinct affinity between each component. It may be noticed that the viscosity of methyl alcohol is very much less than that of its homologues.

Percentage of methyl alcohol.	$\eta$ .	Percentage of methyl alcohol.	$\eta$ .
0	0.008910	51.31	0.01540
6.83	0.01055	52.82	0.01490
10.07	0.01157	55.35	0.01475
21.47	0.01403	58.55	0.01427
35.92	0.01600	61.06	0.01370
37.85	0.01575	66.53	0.01282
40.71	0.01570	73.19	0.01167
46.19	0.01570	77.41	0.01105
49.56	0.01532	100	0.008910

*Acetic Acid and Water.*—This mixture was one of those investigated by Graham, who found a well-marked maximum point corresponding



with that of maximum density at a composition of 23 per cent. of water at 20°. This would be approximately at the point  $1\text{CH}_3\cdot\text{CO}_2\text{H}, 1\text{H}_2\text{O}$ .

Wijkander also noticed that this maximum varied with temperature. Thus, at 30° it is at 19.6 per cent. of acetic acid, whilst at 50° it has shifted to 18 per cent.

The acid used in this investigation contained some water, and its

strength, found by titration and freezing point determinations, was 98.6 per cent. of acetic acid. The viscosity of the pure acid was obtained by extrapolation. Subsequently a sample was obtained by repeated freezing of several litres of the so-called "pure" acid, and was found to be of theoretical purity, freezing at  $16.6^{\circ}$  and boiling at  $117.6^{\circ}$  under 758 mm. pressure.

Percentage of acetic acid.	$\eta$ .	Percentage of acetic acid.	$\eta$ .
0	0.008910	68.85	0.02227
32.10	0.01437	71.96	0.02301
49.44	0.01824	72.04	0.02333
49.74	0.01867	78.16	0.02374
56.99	0.01986	81.66	0.02321
61.86	0.02103	98.6 (sp. gr. = 1.051)	0.01223
		Extrapolation 100	0.01150

### *Discussion of Results.*

The curves obtained divide themselves into two classes. (1) Those approximating to the normal, but giving results not in strict harmony with the law of mixtures, such as those for ethyl acetate—benzene. (2) Those greatly diverging from the normal, having clearly defined maxima or minima, such as ethyl alcohol—water and ethyl alcohol—benzene.

The following conclusions may be drawn :

1. Aqueous solutions give abnormal results. This is true for all cases examined in this paper, which are all solutions of two associated liquids. In this connection, the peculiar behaviour of acetone may be again mentioned. In aqueous solution it affords a maximum point, but with ethyl alcohol a sagged curve of type I is obtained.

2. Wherever chemical affinity is existent to any marked extent between the two liquids, abnormal results occur. Graham's work first brought out this point, and many of the maximum points he observed have been shown to correspond with complexes which may be isolated (Pickering, *Trans.*, 1893, **63**, 1072).

3. Whenever marked abnormalities present themselves, it is to be noted that they do so at or near points of definite molecular composition, but, at the same time, these points of abnormality are not fixed and constant. With change of temperature they shift, and would probably vanish at a sufficiently high temperature. But, on the other hand, at this sufficiently high temperature no such formation of molecular complexes would be possible, no matter how loosely aggregated these might be. It is conceivable that at each tempera-

ture there is a dynamic equilibrium obtained between the opposing tendencies of association and dissociation.

4. In some cases, a liquid mixture gives a minimum point of viscosity. It is difficult to find any adequate reason for this. Wagner's statement that this is due to the diminished concentration of one component does not furnish an explanation. The cause is much more deeply seated, and it most probably betokens some change of molecular aggregation, due either to association or dissociation.

In the case of benzene—alcohol, the benzene complexes possibly break down on the addition of alcohol.

5. As a general rule, compounds containing hydroxyl have a higher viscosity than monomolecular liquids. Water, ethyl alcohol, and acetic acid, although all of low molecular weight, are much more viscous than, for example, ethyl iodide, carbon disulphide, and mercaptan. Again, glycerol and glycol are notably viscous.

Thus the rapid rise of viscosity in the ethyl alcohol—water mixture can be explained by the formation of further loosely-held complexes such as  $3\text{H}_2\text{O}, 1\text{EtOH}$ .

The work is now being extended to other liquid mixtures, specially with unsaturated compounds containing hydroxyl. It is hoped eventually that the results obtained may be applied to the use of aqueous solutions of electrolytes. The author desires to mention that the earlier part of this work was undertaken in collaboration with Mr. W. H. C. Jemmett, and also to thank the Headmaster of Owen's School for the use of the school laboratory, in which this investigation is being pursued.

OWEN'S SCHOOL,  
ISLINGTON.

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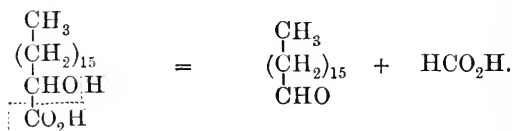
## LXXXIV.—*The Action of Heat on $\alpha$ -Hydroxycarboxylic Acids. Part I. $\alpha$ -Hydroxystearic Acid.*

By HENRY RONDEL LE SUEUR.

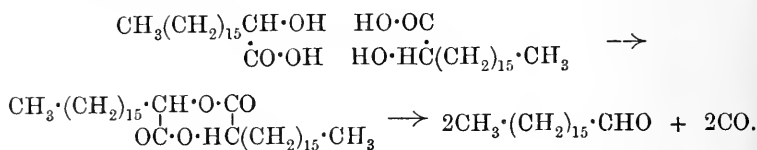
A CONSIDERABLE quantity of  $\alpha$ -hydroxystearic acid having been obtained as a by-product in a research which had for its object the preparation of an isomeride of oleic acid containing the double linking between the  $\alpha$ - and  $\beta$ -carbon atoms, it was deemed advisable to ascertain whether this  $\alpha$ -hydroxystearic acid yielded, like  $\alpha$ -hydroxy-acids in general, a lactide on heating, or whether perchance an unsaturated acid might be formed.

$\alpha$ -Hydroxystearic acid was first prepared by Hell and Sadomsky (*Ber.*, 1891, 24, 2391) by the action of alcoholic potash on  $\alpha$ -bromostearic acid, and was found to melt at 84—85°. If, however, aqueous potassium hydroxide is used, then the acid obtained is beautifully crystalline and melts at 91—92°, and there is no doubt that the substance isolated by Hell and Sadomsky was impure, and probably contaminated with traces of the  $\alpha\beta$ -unsaturated acid.

When  $\alpha$ -hydroxystearic acid is heated in air at a temperature of 270°, it is decomposed into water, carbon monoxide, formic acid, a lactide,  $C_{36}H_{68}O_4$ , and *margaric aldehyde*,  $C_{16}H_{33}\cdot CHO$ , the yield of the latter being 50—60 per cent. of the calculated amount. The aldehyde may be regarded as being formed directly from the  $\alpha$ -hydroxy-acid,



or through the lactide,



Subsequent to the publication of a preliminary note (*Proc.*, 1904, 19, 14) indicating the results then obtained, there appeared in the *Comptes rendus* (1904, 138, 697), and quite recently in the *Bulletin de la Société chimique de Paris* (1904, 31, 483), two communications by E. E. Blaise describing the results of his experiments on the action of heat on some  $\alpha$ -hydroxy-acids of the acetic series, and in these papers he states that the aldehydes result from the decomposition of the lactides and not directly from the  $\alpha$ -hydroxy-acids.

This is certainly not the case with  $\alpha$ -hydroxystearic acid, as was proved by an investigation of the action of heat on the lactide itself, when it was definitely ascertained that the lactide of  $\alpha$ -hydroxystearic acid is only decomposed at a temperature above 260°. Now in the first experiments on the action of heat on  $\alpha$ -hydroxystearic acid, this substance was only heated at 240—250°, yet the yield of aldehyde was almost 50 per cent. of the calculated quantity. Moreover, the decomposition of the lactide into the aldehyde and carbon monoxide is extremely slow at 270—280°; the volume of gas evolved on heating 4.3 grams of the lactide at this temperature for one hour showed that only about one-third of the lactide had been decomposed, yet in the preparation of the aldehyde from 20 grams of  $\alpha$ -hydroxystearic acid

the heating was only continued for one hour, and the yield of aldehyde was from 50 to 60 per cent.

In one experiment, the  $\alpha$ -hydroxystearic acid was heated under 26 mm. pressure, when water was evolved at 170°, but nothing else distilled over below 300°. At this temperature, a small quantity of the substance was removed, and was shown by a melting point determination to consist of almost pure lactide. The heating was then continued, and at 310° gas was evolved and a mixture of aldehyde and lactide distilled over.

One must therefore conclude from these experiments that the aldehyde results from the direct decomposition of the  $\alpha$ -hydroxystearic acid itself, and that although the lactide does yield the aldehyde, yet the latter decomposition only accounts for a small proportion of the total aldehyde formed. The small quantity of formic acid actually obtained and the large amount of carbon monoxide evolved are readily explained on the assumption that the formic acid is immediately decomposed at the high temperature at which the reaction takes place.

These conclusions are based on the results of the investigation of one acid, namely,  $\alpha$ -hydroxystearic acid, and it is possible that although they are true for the higher members of the acetic series, yet they may not be correct for the lower ones, with which Blaise's investigation is chiefly concerned.

That the aldehyde obtained by heating  $\alpha$ -hydroxystearic acid is really the aldehyde of the acid containing one carbon atom less than stearic acid is conclusively proved by the fact that it forms a hydroxycyanide, which, on limited hydrolysis, gives the amide of  $\alpha$ -hydroxystearic acid, and, on complete hydrolysis, the original  $\alpha$ -hydroxystearic acid.

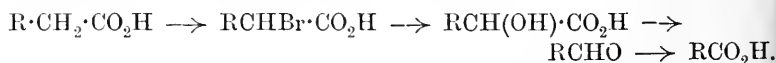
Our knowledge of the properties of the higher aldehydes of the acetic series is very limited, as the few which have been obtained were very incompletely investigated. Krafft (*Ber.*, 1880, 13, 1414), who first prepared lauric, myristic, palmitic, and stearic aldehydes, obtained substances the melting points of which lie very close to those of the acids to which they are related, in the case of lauric aldehyde this constant being actually 0.5° above that of the corresponding acid. This abnormality may possibly be due to the aldehydes having undergone partial polymerisation, for, as is shown in the experimental part of this paper, margaric aldehyde is somewhat prone to undergo this change. An investigation of the action of heat on  $\alpha$ -hydroxymargaric acid will, it is hoped, settle this question.

The acid obtained by the oxidation of margaric aldehyde has been called margaric acid, but whether it is identical with the margaric acid obtained by Krafft (*Ber.*, 1879, 12, 1672) can only be definitely

decided by a comparison of their characteristic derivatives. Their melting points are practically the same, but this is hardly sufficient to enable one to state definitely that they are identical, and it is to be regretted that Krafft did not prepare some characteristic derivatives of his acid, such as the  $\alpha$ -bromo- or  $\alpha$ -hydroxy-derivative, or the amide.

This method of preparing aldehydes would appear to be a general one, especially for the higher members of the acetic series, and, as the yield of aldehyde is good, it may eventually prove to be a very convenient means of obtaining these substances. The preparation of an  $\alpha$ -bromo-acid by Volhard's process (*Annalen*, 1887, 242, 61) and the conversion of this bromo-acid into the  $\alpha$ -hydroxy-derivative are matters of no great difficulty, and the yields obtained are almost theoretical.

The method also affords a ready means of passing from an acid of the acetic series to the next lower homologue:



The author is now engaged in investigating the action of heat on other  $\alpha$ -hydroxy-derivatives of mono- and di-basic  $\alpha$ -hydroxy-acids.

#### EXPERIMENTAL.

The  $\alpha$ -bromostearic acid used in this investigation was prepared from stearic acid (m. p. 68—68·5°) by Hell and Sadomsky's method (*Ber.*, 1891, 24, 2390), and after crystallisation from light petroleum (b. p. 60—80°) melted at 60—61°.

0·2156 gave 0·1120 AgBr. Br = 22·10.

$\text{C}_{18}\text{H}_{35}\text{O}_2\text{Br}$  requires Br = 22·04 per cent.

#### *Preparation of $\alpha$ -Hydroxystearic Acid.*

A solution of 40 grams of pure  $\alpha$ -bromostearic acid, in 400 c.c. of water containing 30 grams of potassium hydroxide, was heated at 100°, the temperature being maintained for 6—7 hours by passing superheated steam into the solution. The resulting potassium salt was decomposed by hot dilute sulphuric acid and the separated acid, which solidified on cooling, was dissolved in ether, the ethereal solution washed with water, dried over calcium chloride, and evaporated to a small bulk, when 24 grams of the acid (m. p. 91—92°) crystallised out. The residue from the ethereal filtrate, when crystallised from chloroform, gave 3 grams more of the pure acid, the yield being 82 per cent.

0.1600 gave 0.4214  $\text{CO}_2$  and 0.1740  $\text{H}_2\text{O}$ .  $\text{C} = 71.83$ ;  $\text{H} = 12.08$ .

$\text{C}_{18}\text{H}_{36}\text{O}_3$  requires  $\text{C} = 72.00$ ;  $\text{H} = 12.00$  per cent.

Pure  $\alpha$ -hydroxystearic acid is somewhat readily soluble in ether or alcohol in the cold, and readily so in hot benzene, chloroform, acetone, or ethyl acetate. It crystallises from ethyl acetate or chloroform in stellar groups of flat needles melting at  $91$ – $92^\circ$ , and not at  $84$ – $85^\circ$ , as stated by Hell and Sadomsky (*loc. cit.*).

*Ethyl  $\alpha$ -Hydroxystearate.*

In attempting to prepare this ester by boiling the silver salt of the acid with ethyl iodide dissolved in anhydrous ether, it was found that the conversion was extremely slow, and the ethereal solution very difficult to filter. Benzene was consequently substituted for ether, and the silver salt (6.5 grams) was boiled with ethyl iodide (4 grams) dissolved in pure benzene for 45 minutes, at the end of which time the conversion was complete. The benzene solution, after filtration from the silver iodide, was evaporated and the residue crystallised from dilute alcohol.

0.1464 gave 0.3900  $\text{CO}_2$  and 0.1598  $\text{H}_2\text{O}$ .  $\text{C} = 72.65$ ;  $\text{H} = 12.12$ .

$\text{C}_{20}\text{H}_{40}\text{O}_3$  requires  $\text{C} = 73.17$ ;  $\text{H} = 12.19$  per cent.

*Ethyl  $\alpha$ -hydroxystearate* is insoluble in water, readily soluble in the cold in ether, chloroform, or benzene, and in alcohol, light petroleum, or acetone on warming. It crystallises from dilute alcohol in long, slender needles melting at  $62$ – $63^\circ$ .

*$\alpha$ -Hydroxystearamide.*

One gram of pure ethyl  $\alpha$ -hydroxystearate and 15 c.c. of alcoholic ammonia were heated together in a sealed tube at  $140^\circ$  for  $7\frac{1}{2}$  hours; the resulting solid was collected, dried on porous plate, and crystallised from alcohol.

0.2122 gave 8.7 c.c. moist nitrogen at  $19^\circ$  and 758 mm.  $\text{N} = 4.70$ .

$\text{C}_{18}\text{H}_{37}\text{O}_2\text{N}$  requires  $\text{N} = 4.68$  per cent.

The amide is insoluble in ether, light petroleum, chloroform, benzene, acetone, or water, and only sparingly soluble in boiling alcohol, from which it crystallises in glistening, white plates melting at  $148$ – $149^\circ$  and resolidifying at  $144^\circ$ .

*Action of Heat on  $\alpha$ -Hydroxystearic Acid.*

Twenty grams of pure  $\alpha$ -hydroxystearic acid were heated in a distillation flask attached to a condenser, and provided with a thermometer, the bulb of which dipped in the substance. The temperature was rapidly raised to  $250^{\circ}$ , at which point the evolution of gas, which began at  $200^{\circ}$ , proceeded vigorously. Finally, the temperature was maintained between  $270^{\circ}$  and  $280^{\circ}$  for one hour, after which the effervescence had almost ceased. A large quantity of carbon monoxide was evolved, and a small amount of a liquid distilled over, which, after filtration from traces of volatilised solid, had a marked acid reaction and readily reduced an ammoniacal solution of silver nitrate. This points to the presence of formic acid, but the amount was too small to admit of its being more definitely identified. If the  $\alpha$ -hydroxystearic acid is pure, then there is no charring, and after heating for one hour the molten mass is at the most only faintly yellow; if, however, the  $\alpha$ -hydroxystearic acid contains a trace of the  $\alpha$ -bromo-acid, then the substance quickly turns black on being heated.

The products resulting from the heating of two quantities of 20 grams each were mixed together and distilled under 26 mm. pressure, when the following fractions were obtained.

205—215°.....	8.5 grams	260—315°.....	12.0 grams
215—260°.....	11.0 „	Undistilled residue.	3.0 „

The fraction boiling at 215—260° was redistilled under 26 mm. pressure, and gave 7.8 grams at 205—215° and 2.0 grams at 215—290°.

The residue was not distilled.

The fraction (b. p. 260—315°) was redistilled under 26 mm. pressure; it yielded 3 grams at 205—215° and 2 grams at 215—260°.

All the fractions boiling between 205° and 215° were mixed together and redistilled under 26 mm. pressure.

195—202°.....	5.7 grams ; m. p. 34—35°.
202—205 .....	7.7 „ m. p. 35.5°.
205—210 .....	4.2 „ m. p. 35—36°.
210—215 .....	1.0 „

The residue was not distilled.

From the melting points of the first three fractions, and also from the fact that on oxidation they gave margaric acid, the portion boiling between  $195^{\circ}$  and  $210^{\circ}$  may be considered as consisting of practically pure

aldehyde; this would correspond with a yield of 52 per cent. The fraction boiling between  $202^{\circ}$  and  $205^{\circ}$  was analysed:

0.1574 gave 0.4630  $\text{CO}_2$  and 0.1898  $\text{H}_2\text{O}$ .  $\text{C} = 80.24$ ;  $\text{H} = 13.39$ .  
 $\text{C}_{17}\text{H}_{34}\text{O}$  requires  $\text{C} = 80.31$ ;  $\text{H} = 13.38$  per cent.

*Margaric aldehyde (heptadecylic aldehyde)* is a white solid melting at  $35\text{--}36^{\circ}$  and boiling at  $203\text{--}204^{\circ}$  under 26 mm. pressure; it has an odour resembling paraffin and is very soluble in cold ether, chloroform, benzene, or light petroleum, not readily soluble in alcohol, acetone, or ethyl acetate in the cold, but dissolving readily on heating, and crystallising in needles from its concentrated solution in light petroleum. Its acetone solution slowly reduces potassium permanganate in the cold, and very readily on warming. A solution of the aldehyde in hot absolute alcohol slowly deposited needle-shaped crystals, which, after drying in the air, melted at  $52^{\circ}$  and were analysed with the following result:

0.1770 gave 0.4934  $\text{CO}_2$  and 0.2112  $\text{H}_2\text{O}$ .  $\text{C} = 76.02$ ;  $\text{H} = 13.25$ .  
 $\text{C}_{17}\text{H}_{34}\text{O}, \text{C}_2\text{H}_5\text{OH}$  requires  $\text{C} = 76.00$ ;  $\text{H} = 13.33$  per cent.

Some of the crystals were then finely powdered and kept in a vacuum desiccator over sulphuric acid until the weight was constant.

0.1734 lost 0.0256.  $\text{C}_2\text{H}_5\cdot\text{OH} = 14.76$ .  
 $\text{C}_{17}\text{H}_{34}\text{O}, \text{C}_2\text{H}_5\cdot\text{OH}$  requires  $\text{C}_2\text{H}_5\cdot\text{OH} = 15.33$  per cent.

The substance, when dried under diminished pressure, melted at  $36^{\circ}$  and was analysed with the following result:

0.1422 gave 0.4168  $\text{CO}_2$  and 0.1692  $\text{H}_2\text{O}$ .  $\text{C} = 79.94$ ;  $\text{H} = 13.22$ .  
 $\text{C}_{17}\text{H}_{34}\text{O}$  requires  $\text{C} = 80.31$ ;  $\text{H} = 13.38$  per cent.

The aldehyde slowly polymerises on keeping, as was shown by the determination of the melting point of a specimen which had been kept for six weeks; this was found not to melt completely until  $55^{\circ}$ , and on treatment with ether left a small amount of insoluble residue, which, after crystallisation from light petroleum, melted at  $77\text{--}78^{\circ}$  and had all the properties of the polymeride mentioned on p. 835.

The *semicarbazone* was obtained by adding semicarbazide hydrochloride (2 mols.) and the requisite amount of potassium acetate dissolved in dilute alcohol to an alcoholic solution of the aldehyde; the solid, which separated after 5 hours, was collected and crystallised from absolute alcohol. It is insoluble in ether, light petroleum, or water, sparingly soluble in chloroform or benzene in the cold, and readily soluble in hot alcohol, from which it separates in aggregates of slender needles melting at  $107\text{--}108^{\circ}$ .

0.1550 gave 18 c.c. moist nitrogen at  $16^{\circ}$  and 743 mm.  $N = 13.24$ .

$C_{18}H_{37}ON_3$  requires  $N = 13.50$  per cent.

The *oxime* was prepared by mixing alcoholic solutions of hydroxylamine (obtained from hydroxylamine hydrochloride and potassium hydroxide) and the aldehyde, heating the mixture on the water-bath for  $2\frac{1}{2}$  hours, and then leaving it overnight. The compound is insoluble in ether or water, sparingly soluble in chloroform, light petroleum, benzene, or alcohol in the cold, but readily soluble in these solvents when heated. It crystallises from ethyl acetate in small, glistening plates melting at  $89.5^{\circ}$ .

0.1544 gave 7.2 c.c. moist nitrogen at  $15^{\circ}$  and 766 mm.  $N = 5.50$ .

$C_{17}H_{35}ON$  requires  $N = 5.20$  per cent.

*Action of Hydrogen Cyanide on Margaric Aldehyde.*—Two grams of the aldehyde were dissolved in pure ether and shaken with 9 c.c. of pure hydrogen cyanide, to which three drops of triethylamine had been added (compare Lapworth, *Trans.*, 1903, 83, 995), and the mixture allowed to remain for two days, when a large amount of solid was found to have separated. The hydrogen cyanide was allowed to evaporate spontaneously, and the solid residue dried on porous plate and crystallised from light petroleum.

0.2106 gave 9.0 c.c. moist nitrogen at  $12^{\circ}$  and 764 mm.  $N = 5.10$ .

$C_{18}H_{35}ON$  requires  $N = 4.98$  per cent.

*$\alpha$ -Hydroxyheptadecyl cyanide*,  $C_{16}H_{33}\cdot CH(OH)\cdot CN$ , is readily soluble in alcohol, ether, chloroform, benzene, or ethyl acetate, and crystallises from light petroleum in small, glistening plates melting at  $61.5$ — $62.5^{\circ}$ .

*Hydrolysis of the Hydroxycyanide.*—The hydroxycyanide was warmed on the water-bath with three times its weight of concentrated hydrochloric acid for 10 minutes. The resulting solid was filtered, and, after drying, melted at  $148^{\circ}$  and had all the properties of  *$\alpha$ -hydroxystearamide* (see page 831); on crystallising from absolute alcohol, it separated in glistening plates melting at  $148$ — $149^{\circ}$ , a melting point which remained unaltered on mixing with  *$\alpha$ -hydroxystearamide*.

The foregoing amide was boiled with a 10 per cent. solution of potassium hydroxide for  $1\frac{1}{2}$  hours, during which time ammonia was evolved; the solution was acidified with dilute sulphuric acid, extracted with ether, and the residue from the ethereal solution crystallised from chloroform, when it separated in flat needles melting at  $91$ — $92^{\circ}$ , which had all the properties of  *$\alpha$ -hydroxystearic acid*, the melting point remaining unaltered on mixing the specimen with this substance.

*Action of Sodium Hydrogen Sulphite on Margaric Aldehyde.*—An ethereal solution of the aldehyde was shaken with a saturated solution

of sodium hydrogen sulphite, when there was an immediate precipitation of the crystalline sodium bisulphite compound, which was filtered, dried on porous plate, washed with ether, and then heated on the water-bath with a 15 per cent. solution of sodium carbonate for  $1\frac{1}{2}$  hours; the whole was then extracted with ether and the ethereal solution evaporated, when a residue was obtained which, as shown by its melting point, consisted for the most part of aldehyde together with a trace of the polymeride mentioned below. The portion insoluble in ether was warmed with a 20 per cent. solution of sulphuric acid for one hour, and, after cooling, was extracted with a large volume of ether. The residue left, after evaporating the solvent, was repeatedly crystallised from light petroleum and analysed:

0.1790 gave 0.5266  $\text{CO}_2$  and 0.2172  $\text{H}_2\text{O}$ .  $\text{C} = 80.23$ ;  $\text{H} = 13.48$ .

$(\text{C}_{17}\text{H}_{34}\text{O})_3$  requires  $\text{C} = 80.31$ ;  $\text{H} = 13.38$  per cent.

The *polymeride* of margaric aldehyde is somewhat readily soluble in cold benzene or chloroform, slightly so in cold ether, acetone, alcohol, or ethyl acetate, and crystallises from light petroleum in aggregates of needles melting at  $77-78^\circ$ . It does not reduce an acetone solution of potassium permanganate, nor does it combine with sodium hydrogen sulphite or hydroxylamine.

Its molecular weight was determined by the freezing point method, using naphthalene as the solvent.

0.9318 in 19.7676 naphthalene gave  $\Delta t = 0.40^\circ$ .  $\text{M. W.} = 813$ .

$(\text{C}_{17}\text{H}_{34}\text{O})_3$  requires  $\text{M. W.} = 762$ .

When the polymeride is heated at  $245-250^\circ$  for a short time, it is almost quantitatively reconverted into the aldehyde melting at  $35-36^\circ$ .

*Lactide of  $\alpha$ -Hydroxystearic Acid.*—The less volatile residues obtained in the purification of the aldehyde (p. 832) were crystallised first from ethyl acetate and finally from a mixture of chloroform and ether.

0.1642 gave 0.4614  $\text{CO}_2$  and 0.1798  $\text{H}_2\text{O}$ .  $\text{C} = 76.64$ ;  $\text{H} = 12.16$ .

$\text{C}_{36}\text{H}_{68}\text{O}_4$  requires  $\text{C} = 76.60$ ;  $\text{H} = 12.06$  per cent.

The *lactide of  $\alpha$ -hydroxystearic acid* is practically insoluble in alcohol, light petroleum, ethyl acetate, or ether in the cold, but dissolves readily on heating; it is very readily soluble in cold chloroform, and crystallises from ether in microscopic needles melting at  $88.5-90.5^\circ$ . It is insoluble in potassium hydroxide, its alcoholic solution is neutral to litmus, and it does not reduce an acetone solution of potassium permanganate even on boiling.

*Hydrolysis of the Lactide.*—The lactide was boiled with a dilute

alcoholic solution of potassium hydroxide for 7 hours, the product was then diluted with water, and, after evaporating off the alcohol, was extracted with chloroform in order to remove any unchanged lactide.

It was then acidified with dilute sulphuric acid, extracted with ether, and the residue obtained on evaporating the solvent crystallised from chloroform, when it melted at 91–92°.

0.1638 gave 0.4304  $\text{CO}_2$  and 0.1738  $\text{H}_2\text{O}$ .  $\text{C} = 71.66$ ;  $\text{H} = 11.79$ .

$\text{C}_{18}\text{H}_{36}\text{O}_3$  requires  $\text{C} = 72.00$ ;  $\text{H} = 12.00$  per cent.

*Action of Heat on the Lactide.*—The pure lactide (4.3 grams) was heated in a distillation flask under atmospheric pressure. At 260° no gas was evolved, nor was there any evidence of decomposition, but at 270° evolution of gas begins, and is somewhat more marked at 275°. The amount of gas evolved after maintaining the temperature at 270–280° for 1 hour was 120 c.c., and at the end of 2½ hours was 300 c.c. at 15° and 760 mm. pressure, this being equivalent to 284 c.c. at 0° and 760 mm. Assuming that the whole of the lactide decomposes into carbon monoxide and aldehyde, the volume of gas should measure 341 c.c. under standard conditions.

This experiment can, however, have no great claim to being strictly quantitative, because the evolved gas was found to contain a considerable amount of carbon dioxide, but, nevertheless, it shows conclusively that the production of the aldehyde from the lactide is extremely slow at 270–280°.

The product resulting from the heating of the lactide was treated with hydroxylamine, when an oxime was isolated which melted at 89° and had all the properties of the oxime of margaric aldehyde.

*Oxidation of Margaric Aldehyde.*—The pure aldehyde (5.3 grams) was dissolved in a mixture of 200 c.c. of acetone and 30 c.c. of water, the solution gently warmed, and treated with finely-powdered potassium permanganate until no further reduction took place. The residue left after evaporation of the acetone was diluted with water and acidified with dilute sulphuric acid, a sufficient amount of sulphurous acid being added to dissolve the manganese dioxide. The precipitated acid was extracted with ether, the ethereal solution washed with water, dried over calcium chloride, and evaporated, when 5.5 grams of crystalline residue (m. p. 59°) were obtained; this was purified by crystallisation from light petroleum.

0.1612 gave 0.4454  $\text{CO}_2$  and 0.1850  $\text{H}_2\text{O}$ .  $\text{C} = 75.36$ ;  $\text{H} = 12.75$ .

$\text{C}_{17}\text{H}_{34}\text{O}_2$  requires  $\text{C} = 75.56$ ;  $\text{H} = 12.59$  per cent.

*Margaric acid* is readily soluble in ether, benzene, or chloroform in the cold, only sparingly so in cold ethyl acetate or alcohol; it crys-

tallises from light petroleum (b. p. 60—88°) in elongated plates which melt at 60—61° and resolidify at 59·5°. The molecular weight was determined by titration with  $N/10$  sodium hydroxide solution, using phenolphthalein as indicator.

0·2392 required 8·9 c.c.  $N/10$  NaOH. M. W. = 269.  $C_{17}H_{34}O_2$  requires M. W. = 270.

The *silver* salt was obtained as a white, gelatinous precipitate by adding a warm alcoholic solution of the sodium salt to a warm alcoholic solution of silver nitrate.

0·1346 gave 0·0386 Ag. Ag = 28·67.

$C_{17}H_{33}O_2Ag$  requires Ag = 28·65 per cent.

The *ethyl* ester, prepared by the action of ethyl iodide on the silver salt in ethereal suspension, is a white, waxy solid which crystallises from dilute alcohol in small plates melting at 28°; it is readily soluble in ether, light petroleum, chloroform, benzene, or ethyl acetate, and insoluble in water.

0·1552 gave 0·4336  $CO_2$  and 0·1800  $H_2O$ . C = 76·20; H = 12·88.

$C_{19}H_{38}O_2$  requires C = 76·51; H = 12·75 per cent.

The *methyl* ester, prepared in a similar manner, is readily soluble in ether, chloroform, light petroleum, benzene, ethyl acetate, or acetone, and crystallises from rectified alcohol in small plates melting at 29°.

0·1550 gave 0·4296  $CO_2$  and 0·1782  $H_2O$ . C = 75·59; H = 12·77.

$C_{18}H_{36}O_2$  requires C = 76·05; H = 12·67 per cent.

The *amide* was prepared by heating the methyl ester with alcoholic ammonia in a sealed tube at 170°.

0·1496 gave 6·8 c.c. moist nitrogen at 15° and 759 mm. N = 5·31.

$C_{17}H_{35}ON$  requires N = 5·20 per cent.

*Margaramide* crystallises from rectified spirits in elongated plates melting at 106°. It is insoluble in ether, light petroleum, or ethyl acetate in the cold, and readily soluble in hot chloroform, ethyl acetate, or alcohol.

*Bromination of Margaric Acid.*—Four grams of the pure acid were intimately mixed with 0·2 gram of dry amorphous phosphorus and brominated with 2 c.c. of dry bromine in the usual manner. The product was poured into cold water, heated on the water-bath until the acid was melted, then allowed to cool, and the solid acid collected, thoroughly washed with water and extracted with ether in the ordinary way, when 5·0 grams of crystalline residue (m. p. 51—51·5°) were

obtained. This product was crystallised from dilute acetic acid and analysed :

0.2112 gave 0.1150 AgBr. Br. = 23.17.

$C_{17}H_{33}O_2Br$  requires Br = 22.92 per cent.

*α-Bromomargaric acid* is readily soluble in alcohol, ether, light petroleum, chloroform, or ethyl acetate in the cold, and crystallises from dilute acetic acid in large, glistening plates melting at  $52.5^\circ$ .

*α-Hydroxymargaric Acid*.—*α*-Bromomargaric acid (2.8 grams) was dissolved in a solution of 2.5 grams of potassium hydroxide in 40 c.c. of water, and the solution heated in boiling water for  $7\frac{1}{2}$  hours. The product was then acidified, extracted with ether, and the ethereal solution washed, dried, and evaporated, when 2.2 grams of a well-defined crystalline residue (m. p.  $87^\circ$ ) was obtained; this substance, when purified by crystallisation from chloroform, separates in plates melting at  $89^\circ$ ; it is somewhat readily soluble in cold ether and almost insoluble in cold alcohol, light petroleum, benzene, or ethyl acetate.

0.1762 gave 0.4574  $CO_2$  and 0.1870  $H_2O$ . C = 70.80; H = 11.79.

$C_{17}H_{34}O_3$  requires C = 71.32; H = 11.88 per cent.

The *silver* salt is a white, amorphous precipitate.

0.2058 gave 0.0566 Ag. Ag = 27.50.

$C_{17}H_{33}O_3Ag$  requires Ag = 27.48 per cent.

It was prepared in the usual way from the sodium salt and silver nitrate.

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## LXXXV.—*The Constituents of Chaulmoogra Seeds.*

By FREDERICK BELDING POWER and FRANK HOWORTH GORNALL.

It has, until quite recently, been assumed that the seeds yielding the so-called "chaulmoogra oil"—a fatty oil, which is largely used in the treatment of leprosy and various skin diseases—are derived from *Gynocardia odorata* (R.Br.), a tree belonging to the family of *Bixaceæ*, and indigenous to the Malayan Peninsula and North-Eastern India (compare "Pharmacographia Indica," Vol. I, p. 142). It is now known, however, that this oil is obtained from the seeds of *Taraktogenos*

*Kurzii* (King), a plant which is a native of Burmah (*Pharm. J.*, 1900, 64, 522, and 1901, 66, 596).

The investigation of chaulmoogra seeds appears hitherto to have been restricted to the fatty oil, obtained from them by expression, and the first chemical examination of the latter is embodied in a paper by Moss (*Year-book of Pharmacy*, 1879, pp. 523—533). The oil examined by Moss was apparently a commercial product, as he gives no indication of having prepared it himself. He states that it had a melting point of  $42^{\circ}$  and a specific gravity at that temperature of 0.930. On hydrolysis, it afforded him 81.1 per cent. of fatty acids, which were considered to consist approximately of "gynocardic acid," 11.7; palmitic acid, 63.0; hypogæic acid, 4.0; and "cocinic" (undecylic) acid, 2.3 per cent., contained in the oil as glyceryl esters, the first two being also present in the free state. The melting point of the mixed acids was  $44^{\circ}$ . The methods adopted for the separation and identification of the above-mentioned acids were not such, however, as to render the results at all conclusive. The so-called "gynocardic acid" is of interest, for the reason that a preparation bearing this name has been an article of commerce for some years, and is employed medicinally. It was stated by Moss to separate from weak alcohol in crystalline plates melting at  $29.5^{\circ}$ . From the results of two analyses, the formula  $C_{14}H_{24}O_2$  was deduced, although it was clearly indicated that additional data would be required in order to determine the correctness of this supposition.

Petit (*J. Pharm. Chim.*, 1892, 26, 445) has published a method for the preparation of "gynocardic acid," and under this name he appears to comprehend that portion of the total fatty acids which is soluble in 70 per cent. alcohol at about  $15^{\circ}$ , and has a melting point of  $29^{\circ}$ , which is practically that assigned to it by Moss.

Schindelmeiser (*Ber. deutsch. pharm. Ges.*, 1904, 14, 164) has published a short paper entitled "Gynocardia Oil," in which he appears to have accepted in general the conclusions of Moss respecting its constituents, but without any confirmatory evidence of their correctness, although he gives the melting point of the "cold-expressed" oil as  $26^{\circ}$ . He also retains the name of gynocardic acid for a substance which was prepared according to Petit's method (*loc. cit.*), and, after purification with ether, melted at  $29.5^{\circ}$ . It was considered probable that the substance thus separated had the formula  $C_{21}H_{40}O_2$ , although this supposition appears to have been based only on a titration and the analysis of a silver salt, and it was shown to be unsaturated. He furthermore assumes, with some reservation, that, besides palmitic, hypogæic, and "cocinic" acids, the crude acids contain a hydroxy-acid, the evidence for the presence of the latter being deduced from a determination of the acetyl value (207.8) and from the high iodine value (110.8).

## EXPERIMENTAL.

An opportunity having been afforded us of obtaining a large quantity of fresh Chaulmoogra seeds, which had been brought into the London market, it was decided to make a complete investigation of them. They were identified as the product of *Turaktogenos Kurzii* (King).

On bruising the seeds, it was observed that a strong odour of hydrocyanic acid was developed. This indicated that it existed in the form of some unstable compound which became hydrolysed through the action of an enzyme. The hydrocyanic acid, after being further identified by qualitative tests, was quantitatively determined as follows: a quantity of the bruised kernels was digested with water for two days in a tightly-closed flask at a temperature of about 23°; steam was then passed through the liquid and the distillate titrated with a decinormal solution of silver nitrate. The amount of hydrocyanic acid corresponded with 0.036 per cent. of the weight of the kernels. When the seeds have been kept for some time, even in a dry place and with the shells unbroken, they no longer furnish hydrocyanic acid in contact with water or by the action of dilute acids.

In operating with several hundredweights of the seeds, the shells, which were first separated, represented 34 per cent. of their weight. The kernels, when subjected to powerful hydraulic pressure, yielded an amount of fixed oil corresponding with 30.9 per cent. of the entire seed. The residual "press-cake" represented 32.2 per cent. of the original weight of the seeds. A portion of the kernels, when completely extracted with ether in a Soxhlet apparatus, afforded 55 per cent. of their weight of fixed oil, corresponding with 38.1 per cent. of the entire seed (having 30.7 per cent. of shells).

*Examination of the "Press-cake."*

This material, when received directly from the press, exhaled a large amount of hydrocyanic acid, and, when kept for a comparatively short time, the compound from which the latter substance was developed became completely decomposed.

*Isolation of a Hydrolytic Enzyme.*

A portion of the press-cake was digested with water at the ordinary temperature and expressed. To the clear, filtered liquid about twice its volume of alcohol was added, when an abundant, light-coloured, flocculent precipitate was obtained, which was collected, washed with a little alcohol, and dried in a desiccator over sulphuric acid. When

dry, it formed a dark brown mass, which could be reduced to a light brown powder. This substance gave the usual reactions characteristic of proteids. It hydrolysed amygdalin with the production of benzaldehyde and hydrocyanic acid, and with potassium myronate it yielded mustard oil. On heating its aqueous solution to boiling, its hydrolytic properties were destroyed. The enzyme has apparently only very little action in effecting the hydrolysis of the fat contained in the seed.

*Search for a Glucoside.*

A quantity of the press-cake was extracted with light petroleum, for the more complete removal of the fatty oil, and subsequently with hot alcohol. After the removal of the alcohol, the extract was mixed with water, purified by basic lead acetate, the excess of lead precipitated by hydrogen sulphide, and the liquid finally concentrated under diminished pressure. A light brown syrup was thus obtained, which developed hydrocyanic acid by contact with the enzyme or other hydrolytic agents, and reduced Fehling's solution on boiling. It afforded an osazone melting at  $205^{\circ}$ , which was evidently a phenylglucosazone.

The syrupy liquid showed no tendency to crystallise, even after a long time, and no crystalline substance could be extracted by treatment with various solvents. A portion of the liquid was boiled in a reflux apparatus with dilute sulphuric acid, and subsequently distilled. The distillate contained a large amount of hydrocyanic acid, but no aldehyde or ketone could be detected. The acid liquid remaining in the flask was extracted with chloroform, which yielded only a very slight syrupy residue. It was then digested with barium carbonate in order to remove the sulphuric acid, filtered, decolorised with animal charcoal, and concentrated under diminished pressure. A viscid liquid containing a large amount of sugar was thus obtained, but no crystalline substance.

Although it has not yet been found possible to isolate either this cyanogenetic compound or any hydrolytic product of an aldehydic or ketonic nature, some further experiments will be made in this direction.

*Volatile Constituents of the Alcoholic Extract.*

A large quantity of the press-cake, which no longer contained any hydrocyanic acid or the compound affording it, was extracted with hot alcohol. After distilling off the alcohol, a soft, dark brown extract was obtained, which had the characteristic odour of the seed and contained a considerable proportion of fatty oil.

Two kilograms of this extract were distilled in steam. The acid distillate, which contained a few oily globules, was extracted with

ether, and on removing the latter a small amount of a highly aromatic, yellow, oily liquid was obtained, which evidently consisted of a mixture of volatile acids and esters, but distilled over too wide a range of temperature to permit of their further investigation. The acid remaining in the distillate was converted into a barium salt, and from this a silver salt was prepared, the chief portion of which was soluble in hot water and crystallised on cooling.

0.1008 gave 0.0652 Ag.  $\text{Ag} = 64.7$ .

$\text{C}_2\text{H}_3\text{O}_2\text{Ag}$  requires  $\text{Ag} = 64.7$  per cent.

This volatile acid was therefore acetic acid.

The extract was then repeatedly treated with hot water, the mixture allowed to cool, and placed on a strainer. A considerable amount of solid fatty matter was thus separated from a dark aqueous liquid, in which some viscid oil was suspended. The solid fat yielded on hydrolysis a quantity of fatty acids, which are probably identical with those contained in the oil expressed from the seeds, and contain a very small amount of formic acid. The aqueous liquid strained from the solid fat was extracted with chloroform, which removed a large amount of oily substance; this was hydrolysed with alcoholic potassium hydroxide, the alcohol removed, the residual potassium salt taken up with water, and the strongly alkaline liquid extracted with ether. The combined ethereal liquids were washed with a little water, dried, and the ether removed. An oily liquid which was thus obtained was fractionally distilled under 18 mm. pressure, and thus resolved into (1) a very small fraction which passed over below  $212^\circ$ ; (2) the principal fraction, which boiled between  $212^\circ$  and  $220^\circ$ ; (3) a small fraction between  $220^\circ$  and  $240^\circ$ , but which passed over chiefly at  $220$ – $225^\circ$ ; and (4) a small amount of dark residue containing a little phytosterol (compare p. 844).

In order to ensure the complete freedom of this neutral liquid from any trace of fatty acids arising from the dissociation of their alkali salts in the process for its separation, the above-mentioned fraction,  $212$ – $220^\circ/18$  mm., was dissolved in ether and the solution shaken out many times with a concentrated solution of potassium hydroxide. The ethereal liquid was then washed, dried, the ether removed, and the residual, light yellow oil again distilled. It passed over almost entirely at  $213$ – $220^\circ/18$  mm., as a nearly colourless, odourless liquid, the greater portion distilling at  $214$ – $215^\circ/18$  mm. A portion boiling at the latter temperature was taken for analysis and the determination of its constants.

0.1403 gave 0.3967  $\text{CO}_2$  and 0.1455  $\text{H}_2\text{O}$ .  $\text{C} = 77.1$ ;  $\text{H} = 11.5$ .

0.1053 „ 0.2989  $\text{CO}_2$  „ 0.1100  $\text{H}_2\text{O}$ .  $\text{C} = 77.4$ ;  $\text{H} = 11.6$ .

0.1087 gave 0.3077  $\text{CO}_2$  and 0.1139  $\text{H}_2\text{O}$ .  $\text{C} = 77.2$ ;  $\text{H} = 11.6$ .

$\text{C}_{18}\text{H}_{32}\text{O}_2$  requires  $\text{C} = 77.1$ ;  $\text{H} = 11.4$  per cent.

Its density was 0.9066 at  $16^\circ/16^\circ$ . In a 1 dm. tube, it gave  $\alpha_D + 38.27'$ , whence  $[\alpha]_D + 42.4^\circ$ .

This substance, on account of its method of isolation and purification, can be neither an acid nor a lactone. As it could be recovered unchanged after boiling with acetic anhydride and sodium acetate, it is also not an alcohol. It is unsaturated, and would appear to contain one ethylenic linking.

0.6460 required 0.5997 iodine.  $\text{I} = 92.8$ .

$\text{C}_{18}\text{H}_{32}\text{O}_2$ , with one ethylenic linking, requires  $\text{I} = 90.7$  per cent.

It has not yet been definitely determined to what class of compounds this substance belongs, but from some results which will be communicated later it may be stated that in all probability it is either an unsaturated, open chain diketone or a partly cyclic, unsaturated keto-ether. The occurrence in nature of substances conforming with either of these types has apparently not hitherto been observed.

The strongly alkaline solution of potassium salts from which the above-described neutral liquid had been extracted by ether was acidified with sulphuric acid, when some solid fatty acids separated. On distilling the liquid, a volatile acid was obtained which was converted into its barium salt, the reactions and analysis of the latter showing it to be formic acid.

### *The Fatty Oil (Chaulmoogra Oil).*

At the ordinary temperature, this is a soft solid, having a faintly yellow colour and a characteristic odour. Its constants were determined with the following results.

	Expressed oil.	Oil extracted by ether.
Melting point .....	22—23°	22—23°
Specific gravity .....	{ 0.951 at 25° 0.940 at 45°	{ 0.952 at 25° 0.942 at 45° }
$[\alpha]_D^{15^\circ}$ .....	+52.0°	+51.3°
Acid value .....	23.9	9.5
Saponification value ...	213.0	208.0
Iodine value.....	103.2	104.4

*Hydrolysis of the Fatty Oil. Identification of Phytosterol and Glycerol, and Separation of the Fatty Acids*

One hundred grams of the expressed oil were hydrolysed by boiling with an excess of alcoholic potash. After the removal of some of the alcohol, the dark liquid was mixed with sand and the mixture heated until quite dry, when it was brought into a Soxhlet apparatus and extracted with light petroleum. After the removal of the petroleum, a residue was obtained which consisted of a small amount of a crystalline substance associated with some light yellow, gummy matter having a cinnamon-like odour. By dissolving the product in warm ethyl alcohol and cooling the solution, the crystalline substance was separated from the amorphous matter, and, after several crystallisations from ethyl alcohol, was obtained in the form of white, glistening needles melting at  $132^{\circ}$ .

0.0694 gave 0.2128  $\text{CO}_2$  and 0.0760  $\text{H}_2\text{O}$ .  $\text{C} = 83.6$ ;  $\text{H} = 12.2$ .

0.1861 ,, 0.5704  $\text{CO}_2$  ,, 0.2007  $\text{H}_2\text{O}$ .  $\text{C} = 83.6$ ;  $\text{H} = 12.0$ .

$\text{C}_{26}\text{H}_{44}\text{O}$  requires  $\text{C} = 83.9$ ;  $\text{H} = 11.8$  per cent.

The substance thus has the formula and melting point of phytosterol, and its identity was further confirmed by the colour reactions characteristic of the cholesterol group.

For the identification of glycerol as a product of hydrolysis of the oil, the mixture in the Soxhlet apparatus was extracted several times with hot water. The cold, alkaline, aqueous liquid was then acidified with sulphuric acid, and the fatty acids, which separated as a nearly white, solid cake, were collected by filtration. The acid filtrate was then treated with barium carbonate, in order to remove the sulphuric acid, and evaporated. By subsequently mixing the residue with alcohol, again concentrating as far as possible and repeating this operation several times, a residue was obtained from which alcohol extracted 6 grams of glycerol, which, on distillation under 18 mm. pressure, passed over at  $185^{\circ}$ .

0.0898 gave 0.1270  $\text{CO}_2$  and 0.0710  $\text{H}_2\text{O}$ .  $\text{C} = 38.6$ ;  $\text{H} = 8.8$ .

$\text{C}_3\text{H}_5\text{O}_3$  requires  $\text{C} = 39.1$ ;  $\text{H} = 8.7$  per cent.

*The Fatty Acids.*

The foregoing solid fatty acids were dissolved in ether, the solution dried, and the ether removed; the residue, which soon formed a solid cake, weighed 90 grams. For the determination of the constants of the mixture of fatty acids thus obtained, a quantity of the dried product was first heated in a steam oven and then exposed over paraffin

wax in a vacuum desiccator in order to eliminate the last trace of ether. The solidified product then melted at 44—45°, had a specific rotatory power  $[\alpha]_D +52.6^\circ$  in chloroform, the "acid value" 215, and the "iodine value" 103.2.

The absence of hydroxy-acids in this mixture was proved by the fact that, on treatment with acetic anhydride according to Lewkowitsch's method (*J. Soc. Chem. Ind.*, 1890, 9, 846), no acetylation took place.

*Fractional Crystallisation of the Fatty Acids.*

For the examination of the fatty acids, which obviously represented a mixture of substances, 7250 grams were dissolved in 20 litres of hot 94 per cent. alcohol. When left overnight, the cold solution yielded 2300 grams of a distinctly crystalline acid. This was again crystallised, in the first instance from alcohol (90 per cent.), and finally from light petroleum, when 1100 grams of an acid were obtained which separated from the latter solvent in glistening leaflets melting at 68°, and this melting point remained unaltered by further crystallisations from a variety of solvents.

By removing the solvent from the first of the last two mother liquors, 800 grams of residue remained. In order to eliminate a small amount of resinous matter, and thus obtain the substance in a form better adapted for analysis and the determination of constants, a portion was dissolved in an alcoholic solution of potassium hydroxide, the solution concentrated as far as possible, the potassium salt dissolved in water, and the solution extracted several times with light petroleum. The aqueous solution was then acidified, the liberated acids taken up with ether, the ethereal solution washed, dried, and the solvent removed, in the first instance by distillation, and subsequently by exposure of the warm, melted acid in a vacuum desiccator over paraffin wax. The white, solid acids thus obtained melted at 34—35°.

The last-mentioned, petroleum mother liquor was also treated in a similar manner. The residue, after the removal of the solvent, weighed 400 grams, and, after purification from resinous matter, the melting point of the fraction was 59—61°.

Having initially separated a large amount of an individual acid (m. p. 68°), which will subsequently be described, the first mother liquor was diluted with a small volume of water, which precipitated a quantity of substance, and this was again dissolved by raising the temperature a few degrees. On cooling, there separated from this solution a fraction of solid acids which weighed 2500 grams; a portion of this product, after the removal of some resinous matter, melted at 43—44°. The mother liquor from this fraction was then diluted with

sufficient water to precipitate the whole of the acids remaining in solution, which separated as a somewhat oily cake; the latter was then subjected to pressure, and was thus separated into 1500 grams of solid acids, which, after purification, melted at  $36-38^{\circ}$ , and 950 grams of a light brown oil.

*Identification of Palmitic Acid.*

The 950 grams of oil obtained by expression, as stated above, were fractionally distilled, when practically the whole passed over between  $210^{\circ}$  and  $235^{\circ}/10$  mm. A fraction which distilled between  $210^{\circ}$  and  $220^{\circ}/10$  mm. was separated; it passed over as a slightly yellow oil, which, however, solidified on cooling. In order to remove some adhering oil, it was drained at the pump and finally on porous earthenware. The dry acid was then crystallised, first from methyl alcohol, then from acetone, when it melted at  $62-63^{\circ}$ , and finally from ethyl acetate, when its melting point remained unchanged. It was definitely shown to be palmitic acid by analysis and titration, by the estimation of silver in its silver salt, as also by the fact that it was optically inactive and behaved as a saturated compound towards bromine and permanganate.

*Isolation of a New Unsaturated Acid, Chaulmoogric Acid,  $C_{18}H_{32}O_2$ .*

In the course of the fractional crystallisation of the fatty acids (p. 845), the isolation of a large quantity of an individual substance, melting at  $68^{\circ}$ , was noted.

0.1416 gave 0.3976  $CO_2$  and 0.1460  $H_2O$ .  $C=76.6$ ;  $H=11.5$ .

0.1432 „ 0.4046  $CO_2$  „ 0.1500  $H_2O$ .  $C=77.0$ ;  $H=11.6$ .

0.1344 „ 0.3783  $CO_2$  „ 0.1388  $H_2O$ .  $C=76.8$ ;  $H=11.4$ .

$C_{18}H_{32}O_2$  requires  $C=77.1$ ;  $H=11.4$  per cent.

The silver salt was prepared from an alcoholic solution of the ammonium salt, and formed a white, amorphous precipitate, which was washed successively with water, alcohol, and ether.

0.1280 gave 0.0356 Ag.  $Ag=27.8$ .

0.0884 „ 0.1804  $CO_2$ , 0.0666  $H_2O$ , and 0.0246 Ag.

$C=55.7$ ;  $H=8.4$ ;  $Ag=27.8$ .

$C_{18}H_{31}O_2Ag$  requires  $C=55.8$ ;  $H=8.0$ ;  $Ag=27.9$  per cent.

0.6914, in alcohol, required NaOH equivalent to 24.6 c.c. of a decinormal solution, and 0.8022 required 28.6 c.c., which are the calculated amounts for  $C_{18}H_{32}O_2$ .

It is thus quite evident that the acid melting at  $68^{\circ}$  has the formula  $C_{18}H_{32}O_2$ , and is isomeric with linolic acid, which belongs to the series  $C_nH_{2n-4}O_2$ . All the known acids of this series are

unsaturated to the extent of two ethylenic linkings, or, in other words, combine directly with four atomic proportions of bromine or iodine. They are, therefore, all open chain, unsaturated acids. The acid melting at  $68^{\circ}$ , however, combines directly with only two atomic proportions of bromine or iodine.

0.7428 absorbed 0.6697 iodine.  $I = 90.1$ .

$C_{18}H_{32}O_2$ , with one ethylenic linking, requires  $I = 90.6$ .

$C_{18}H_{32}O_2$ , with two ethylenic linkings, requires  $I = 181.2$  per cent.

This fact, together with some results recorded in the following paper, shows that this acid, although having the general formula  $C_nH_{2n-4}O_2$ , contains only one ethylenic linking; it, therefore, must necessarily contain a closed carbon ring. In view of this conclusion, it became clear that it represents a new substance, since no acid of an alicyclic nature has hitherto been isolated from the fats or oils. On account of the vernacular name of the oil from which it has been isolated, it has been decided to designate this new acid as *chaulmoogric acid*.

Another interesting character of the acid, which again differentiates it from any of the known acids of the same formula, is its optical activity.

A solution containing 3.892 grams in 100 c.c. of chloroform gave  $\alpha_D + 2^{\circ}11'$  in a 1 dm. tube, whence  $[\alpha]_D + 56^{\circ}$ .

Chaulmoogric acid, as compared with its known isomerides, is a very stable substance; it can be distilled without the slightest decomposition, and passes over at  $247-248^{\circ}$  (corr.)/20 mm. as a colourless oil, which soon solidifies to a solid, crystalline mass. The distilled acid was analysed.

0.1258 gave 0.3545  $CO_2$  and 0.1315  $H_2O$ .  $C = 76.9$ ;  $H = 11.6$ .

$C_{18}H_{32}O_2$  requires  $C = 77.1$ ;  $H = 11.4$  per cent.

Chaulmoogric acid is readily oxidised by cold potassium permanganate or nitric acid. It is also readily attacked by concentrated sulphuric acid, with much decomposition and the evolution of sulphur dioxide.

It is sparingly soluble in, and can readily be crystallised from, the usual organic solvents, with the exception of chloroform and ether, in which it is easily soluble even in the cold. It is also soluble in aqueous solutions of the alkalis, forming salts which have the character of soaps.

A number of the metallic salts of the acid have been prepared and analysed. They are of the types  $C_{18}H_{31}O_2M'$ ,  $(C_{18}H_{31}O_2)_2M''$ , and  $(C_{18}H_{31}O_2)_3M'''$  respectively, but in the case of the potassium salts an acid salt having the formula  $C_{18}H_{31}O_2K, 2C_{18}H_{32}O_2$  is formed, besides the normal salt,  $C_{18}H_{31}O_2K$ . Such acid potassium salts of monobasic acids are also known in the cases of palmitic and stearic acids,

The *ammonium* salt,  $C_{18}H_{31}O_2 \cdot NH_4$ , crystallises from alcohol in pearly leaflets. On heating at  $110^\circ$  or on boiling its aqueous solution, it is readily dissociated into ammonia and chaulmoogric acid.

0.3907, on heating, lost  $0.0237 NH_3$ .  $NH_3 = 6.1$ .

$C_{18}H_{35}O_2N$  requires  $NH_3 = 5.7$  per cent.

The *normal potassium* salt,  $C_{18}H_{31}O_2K$ , was obtained as an amorphous powder by precipitation with ether from a strongly alkaline alcoholic solution.

0.3054 gave  $0.0866 K_2SO_4$ .  $K = 12.7$ .

$C_{18}H_{31}O_2K$  requires  $K = 12.3$  per cent.

The *acid potassium* salt,  $C_{18}H_{31}O_2K, 2C_{18}H_{32}O_2$ , forms needles from a neutral aqueous solution.

0.2118 gave  $0.0226 K_2SO_4$ .  $K = 4.8$ .

$C_{18}H_{31}O_2K, 2C_{18}H_{32}O_2$  requires  $K = 4.4$  per cent.

The *sodium* salt resembled the potassium salt, but was more difficult to prepare.

The *lithium* salt,  $C_{18}H_{31}O_2Li$ , prepared by boiling an alcoholic solution of the acid with lithium carbonate, forms fern-like crystals, which are fairly soluble in hot, but only slightly so in cold, dilute alcohol.

0.6886 gave  $0.1316 Li_2SO_4$ .  $Li = 2.4$ .

$C_{18}H_{31}O_2Li$  requires  $Li = 2.4$  per cent.

The following salts were all prepared from a warm alcoholic solution of the potassium salt by precipitation with a soluble salt of the respective metal.

The *calcium* salt,  $(C_{18}H_{31}O_2)_2Ca$ , *barium* salt,  $(C_{18}H_{31}O_2)_2Ba$ , and *strontium* salt,  $(C_{18}H_{31}O_2)_2Sr$ , are white, amorphous powders.

0.3136 gave  $0.0664 CaSO_4$ .  $Ca = 6.2$ .

0.2842 „  $0.0920 BaSO_4$ .  $Ba = 19.0$ .

0.2856 „  $0.0792 SrSO_4$ .  $Sr = 13.2$ .

$C_{36}H_{62}O_4Ca$  requires  $6.7$ ;  $C_{36}H_{62}O_4Ba$  requires  $19.8$ ;

$C_{36}H_{62}O_4Sr$  requires  $13.6$  per cent.

The *magnesium* salt,  $(C_{18}H_{31}O_2)_2Mg, 2H_2O$ , separates in needles.

0.3028 lost, at  $100^\circ$ ,  $0.0178 H_2O$  and gave  $0.0184 MgO$ .  $H_2O = 5.9$ ;  
 $Mg = 3.7$ .

$C_{36}H_{62}O_4Mg, 2H_2O$  requires  $H_2O = 5.8$ ;  $Mg = 3.9$  per cent.

The *zinc* salt,  $(C_{18}H_{31}O_2)_2Zn$ , forms small, colourless crystals.

0.3174 gave  $0.0410 ZnO$ .  $Zn = 10.4$ .

$C_{36}H_{62}O_4Zn$  requires  $Zn = 10.5$  per cent.

The *ferric* salt,  $(C_{18}H_{31}O_2)_3Fe$ , is a light brown, amorphous powder.

0.2282 gave 0.0204  $Fe_2O_3$ .  $Fe = 6.3$ .

$C_{54}H_{93}O_6Fe$  requires  $Fe = 6.3$  per cent.

The *manganous* salt,  $(C_{18}H_{31}O_2)_2Mn$ , is a nearly white, amorphous powder.

0.2550 gave 0.0318  $Mn_2O_4$ .  $Mn = 9.0$ .

$C_{36}H_{62}O_4Mn$  requires  $Mn = 9.0$  per cent.

The *lead* salt,  $(C_{18}H_{31}O_2)_2Pb$ , is a white, amorphous powder.

0.3066 gave 0.1226  $PbSO_4$ .  $Pb = 27.3$ .

$C_{36}H_{62}O_4Pb$  requires  $Pb = 27.1$  per cent.

The *copper* salt,  $(C_{18}H_{31}O_2)_2Cu$ , is a light green powder.

0.3936 gave 0.0490  $CuO$ .  $Cu = 9.9$ .

$C_{36}H_{62}O_4Cu$  requires  $Cu = 10.2$  per cent.

*Intermediate Fractions obtained in the Separation of Palmitic and Chaulmoogric Acids (p. 845).*

*Fraction melting at 59—61°.*—This fraction was found to boil between 230° and 240°/11—12 mm.

10.2 grams in 100 c.c. of chloroform gave  $\alpha_D + 2.9'$  in a 50 mm. tube, whence  $[\alpha]_D + 42.2^\circ$ .

0.1032 gave 0.2868  $CO_2$  and 0.1062  $H_2O$ .  $C = 75.7$ ;  $H = 11.4$ .

0.0802 „ 0.2220  $CO_2$  „ 0.0814  $H_2O$ .  $C = 75.5$ ;  $H = 11.3$ .

$C_{18}H_{32}O_2$  requires  $C = 77.1$ ;  $H = 11.4$  per cent.

$C_{16}H_{32}O_2$  „  $C = 75.0$ ;  $H = 12.5$  „

$C_{16}H_{28}O_2$  „  $C = 76.2$ ;  $H = 11.1$  „

$C_{14}H_{24}O_2$  „  $C = 75.0$ ;  $H = 10.7$  „

0.9244 required NaOH equivalent to 35.3 c.c. of a decinormal solution, instead of 33 c.c. or 36.1 c.c., the calculated amounts for  $C_{18}H_{32}O_2$  or  $C_{16}H_{32}O_2$  respectively.

0.6944 required 0.4673 iodine.  $I = 67.3$ .

$C_{18}H_{32}O_2$ , with one ethylenic linking, requires  $I = 90.6$ .

$C_{16}H_{28}O_2$ , „ „ „ „  $I = 100.7$  per cent.

From a consideration of these results, this fraction probably contains chaulmoogric and palmitic acids, together with an acid or acids of lower carbon content than  $C_{18}$ , and belonging to the series  $C_nH_{2n-4}O_2$  with one ethylenic linking.

*Fraction melting at 34—35°.*—This fraction distilled between 218° and 225°/11—12 mm.

14.93 grams in 100 c.c. of chloroform gave  $\alpha_D + 3^\circ 5'$  in a 50 mm. tube, whence  $[\alpha]_D + 41.5^\circ$ .

0.0870 gave 0.2398  $\text{CO}_2$  and 0.0886  $\text{H}_2\text{O}$ .  $\text{C} = 75.2$ ;  $\text{H} = 11.3$ .

0.1006 „ 0.2774  $\text{CO}_2$  „ 0.1016  $\text{H}_2\text{O}$ .  $\text{C} = 75.2$ ;  $\text{H} = 11.2$  per cent.

1.0014 required NaOH equivalent to 39 c.c. of a decinormal solution, which is the calculated amount for  $\text{C}_{16}\text{H}_{32}\text{O}_2$ .

0.6972 required 0.6163 iodine.  $\text{I} = 88.4$  per cent.

From these data it is probable that this fraction consists largely of an acid or acids having the formula  $\text{C}_{16}\text{H}_{28}\text{O}_2$  or  $\text{C}_{14}\text{H}_{24}\text{O}_2$ , belonging to the series  $\text{C}_n\text{H}_{2n-4}\text{O}_2$  with one ethylenic linking.

*Fraction melting at  $43-44^\circ$ .*—This fraction distilled between  $224^\circ$  and  $234^\circ/11-12$  mm.

12.66 grams in 100 c.c. of chloroform gave  $\alpha_D + 3^\circ 34'$  in a 50 mm. tube, whence  $[\alpha]_D + 56.3^\circ$ .

0.0884 gave 0.2430  $\text{CO}_2$  and 0.0884  $\text{H}_2\text{O}$ .  $\text{C} = 75.0$ ;  $\text{H} = 11.1$ .

0.1173 „ 0.3243  $\text{CO}_2$  „ 0.1172  $\text{H}_2\text{O}$ .  $\text{C} = 75.4$ ;  $\text{H} = 11.1$  per cent.

1.0962 required NaOH equivalent to 42.6 c.c. of a decinormal solution, instead of 39.1 c.c. or 42.8 c.c., the calculated amounts for  $\text{C}_{18}\text{H}_{32}\text{O}_2$  or  $\text{C}_{16}\text{H}_{32}\text{O}_2$  respectively.

0.6948 required 0.6700 iodine.  $\text{I} = 96.4$  per cent.

The probable composition of this fraction may be indicated by the remarks appended to the one preceding it.

*Fraction melting at  $36-38^\circ$ .*—This fraction distilled between  $225^\circ$  and  $235^\circ/11-12$  mm.

11.6 grams in 100 c.c. of chloroform gave  $\alpha_D + 2^\circ 54'$  in a 50 mm. tube, whence  $[\alpha]_D + 50^\circ$ .

0.1060 gave 0.2922  $\text{CO}_2$  and 0.1054  $\text{H}_2\text{O}$ .  $\text{C} = 75.2$ ;  $\text{H} = 11.0$ .

0.1070 „ 0.2940  $\text{CO}_2$  „ 0.1054  $\text{H}_2\text{O}$ .  $\text{C} = 74.9$ ;  $\text{H} = 11.0$  per cent.

1.0002 required NaOH equivalent to 37.5 c.c. of a decinormal solution, instead of 35.7 c.c. or 39 c.c., the calculated amounts for  $\text{C}_{18}\text{H}_{32}\text{O}_2$  or  $\text{C}_{16}\text{H}_{32}\text{O}_2$  respectively.

0.6942 required 0.6460 iodine.  $\text{I} = 93.1$  per cent.

From these data, the composition of this fraction would appear to be essentially that of the preceding one.

*The Oily Acid separated by Pressure.*—This fraction distilled between  $218^\circ$  and  $227^\circ/10$  mm. as an almost colourless oil, which, on cooling, formed a nearly solid cake melting at  $20^\circ$ .

14.14 grams in 100 c.c. of chloroform gave  $\alpha_D + 3^\circ 4'$  in a 50 mm. tube, whence  $[\alpha]_D + 43.4^\circ$ .

0.0820 gave 0.2302 CO<sub>2</sub> and 0.0826 H<sub>2</sub>O. C = 76.6 ; H = 11.2.

0.0858 „ 0.2408 CO<sub>2</sub> „ 0.0864 H<sub>2</sub>O. C = 76.5 ; H = 11.2 per cent.

0.9936 required NaOH equivalent to 37.6 c.c. of a decinormal solution, instead of 35.5 c.c. or 38.8 c.c., the calculated amounts for C<sub>18</sub>H<sub>32</sub>O<sub>2</sub> or C<sub>16</sub>H<sub>32</sub>O<sub>2</sub> respectively.

0.6984 required 0.8976 iodine. I = 128.5 per cent.

It has already been shown that palmitic acid is contained in this fraction (p. 849). The high percentage of iodine required indicates, however, that it contains a considerable proportion of an acid or acids of the series C<sub>n</sub>H<sub>2n-4</sub>O<sub>2</sub>, but with two ethylenic linkings.

From the results of the examination of the foregoing intermediate fractions, it would thus appear that they contain, besides chaulmoogric acid and a small proportion of palmitic acid, some lower homologues of the former, of the series C<sub>n</sub>H<sub>2n-4</sub>O<sub>2</sub>, on the one hand with a closed ring and one ethylenic linking, and on the other with two ethylenic linkings.

We cannot confirm the statement of Moss (*loc. cit.*) that undecyclic acid ("cocinic" acid) is a constituent of chaulmoogra oil, nor have we been able to isolate an individual acid which would correspond with hypogæic acid. From our experience in the separation of the acids of chaulmoogra oil, it may confidently be stated that the "gynocardic acid" of Moss, and of subsequent investigators, does not represent an individual substance.

We have prepared, and are at present investigating, the fatty oil from the seeds of *Gynocardia odorata* (R.Br.); it appears to be very different in character from that obtained from the seeds of *Taraktogenos Kurzii* (King), which we have proved to be identical with the chaulmoogra oil of commerce.

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## LXXXVI.—*The Constitution of Chaulmoogric Acid.* *Part I.*

By FREDERICK BELDING POWER and FRANK HOWORTH GORNALL.

IN the preceding paper on the constituents of chaulmoogra seeds, from *Taraktogenos Kurzii* (King), the isolation of a new, unsaturated, fatty acid, melting at 68°, was described. This substance, designated as *chaulmoogric acid*, was shown to have the formula C<sub>18</sub>H<sub>32</sub>O<sub>2</sub>, and

would thus at first sight appear to belong to the series  $C_nH_{2n-4}O_2$ , which includes its isomerides linolic and tariric acids, both of which also occur in fatty oils. These two acids, however, form tetrabromides, and, under certain conditions, combine respectively with four atomic proportions of iodine, whereas chaulmoogric acid interacts with only two atomic proportions of these elements. It therefore became evident that chaulmoogric acid possesses only one ethylenic linking, and must necessarily contain in its structure a closed ring, a conclusion which has been amply borne out by further investigation. It is the possession of the latter feature which specially differentiates chaulmoogric acid from any of the known naturally occurring fatty acids.

With the object of eventually elucidating the constitution of chaulmoogric acid, a number of its derivatives have been prepared and studied, and some of the results thus far obtained are given in this communication.

When chaulmoogric acid is treated with methyl alcohol and hydrogen chloride, *methyl chaulmoograte*,  $C_{17}H_{31} \cdot CO_2Me$ , is produced, *ethyl chaulmoograte*,  $C_{17}H_{31} \cdot CO_2Et$ , being obtained in a similar manner. *Chaulmoogramide*,  $C_{17}H_{31} \cdot CO \cdot NH_2$ , was prepared according to Aschan's method (*Ber.*, 1898, 31, 2344).

When chaulmoogric acid is treated with hydrogen bromide in glacial acetic acid, the optically inactive *bromodihydrochaulmoogric acid*,  $C_{17}H_{32}Br \cdot CO_2H$  (m. p. 36—38°), is produced.

When ethyl chaulmoograte, in chloroform solution, is treated in the cold with an excess of bromine, it readily combines with two atomic proportions of the latter, forming *ethyl dibromodihydrochaulmoograte*,  $C_{17}H_{31}Br_2 \cdot CO_2Et$ , which is a yellow oil.

When chaulmoogric acid was treated with sodium and amyl alcohol, its ethylenic linking was not resolved, but *chaulmoogryl alcohol*,  $C_{18}H_{33} \cdot OH$ , and *chaulmoogryl chaulmoograte*,  $C_{17}H_{31} \cdot CO_2 \cdot C_{18}H_{33}$ , were obtained. The former is evidently produced by the reduction of the esters of chaulmoogric acid, which would be formed in small amount by the interaction of the acid and the amyl alcohol prior to the introduction of the sodium (compare Bouveault and Blanc, *Compt. rend.*, 1903, 137, 328). The formation of chaulmoogryl chaulmoograte took place during the subsequent fractional distillation of the mixture of chaulmoogryl alcohol and unchanged chaulmoogric acid.

When, however, bromodihydrochaulmoogric acid is treated with zinc dust and alcohol, or chaulmoogric acid with hydriodic acid and phosphorus, the saturated compound, *dihydrochaulmoogric acid*,  $C_{17}H_{33} \cdot CO_2H$ , is formed; the *methyl ester*,  $C_{17}H_{33} \cdot CO_2Me$ , of the latter acid was also prepared. The last-mentioned method of reduc-

tion also yielded a hydrocarbon, *chaulmoogrene*, which, on analysis, gave figures agreeing with the formula  $C_{18}H_{34}$ .

When chaulmoogric acid was oxidised with cold permanganate in amount equivalent to 1 atomic proportion of oxygen, *dihydroxy-dihydrochaulmoogric acid*,  $C_{17}H_{31}(OH)_2 \cdot CO_2H$ , was isolated. When, however, an amount of permanganate equivalent to 4—5 atomic proportions of oxygen was employed, a mixture of several acids was obtained, from which were isolated formic acid and two dibasic acids having the formulæ  $C_{15}H_{28}(CO_2H)_2$  (*ethyl ester*,  $C_{15}H_{28}(CO_2Et)_2$ ) and  $C_{15}H_{28}O(CO_2H)_2$ . The *ethyl ester* of the latter acid,  $C_{15}H_{28}O(CO_2Et)_2$ , was also prepared.

Dr. W. H. Perkin, sen., very kindly determined for us the magnetic rotation and refractive power of ethyl chaulmoograte. The molecular rotatory power of this compound was found to approximate very closely to the calculated value for an unsaturated substance having the formula  $C_{20}H_{36}O_2$ , possessing a closed ring and one ethylenic linking, the latter being contained in an allyl group.

Dr. Perkin's suggestion that chaulmoogric acid might contain an allyl-group was made prior to the isolation of formic acid and the two acids having the formulæ  $C_{17}H_{30}O_4$  and  $C_{17}H_{30}O_5$ , and these results have therefore confirmed the correctness of this assumption.

#### EXPERIMENTAL.

##### *Methyl Chaulmoograte*, $C_{17}H_{31} \cdot CO_2Me$ .

Fifteen grams of chaulmoogric acid were dissolved in 30 grams of methyl alcohol and a current of hydrogen chloride passed into the warm solution during two hours. The ester soon separated as an oily layer, which, on cooling, became solid; water was then added and the whole extracted with ether. The ethereal solution was washed successively with water, then several times with 10 per cent. aqueous sodium carbonate, and finally with water, dried, the ether removed, and the residual oil distilled under diminished pressure. It practically all passed over at  $227^\circ$  corr./20 mm. as a colourless oil, which, on cooling, formed a solid mass of needles, melting at  $22^\circ$ .

0.1185 gave 0.3368  $CO_2$  and 0.1265  $H_2O$ .  $C = 77.5$ ;  $H = 11.8$ .

0.1209 „ 0.3422  $CO_2$  „ 0.1290  $H_2O$ .  $C = 77.2$ ;  $H = 11.8$ .

$C_{19}H_{34}O_2$  requires  $C = 77.6$ ;  $H = 11.6$  per cent.

$d_{25}^{25} = 0.9119$ ;  $\alpha_D + 46.4'$  in a 1 dcm. tube, whence  $[\alpha]_D + 50.5^\circ$ . Five grams in 100 c.c. of chloroform gave  $\alpha_D + 1.14'$  in a 50 mm. tube, whence  $[\alpha]_D^{15} + 50^\circ$ .

*Ethyl Chaulmoograte*,  $C_{17}H_{31}\cdot CO_2Et$ .

Ethyl chaulmoograte was prepared in the same manner as the methyl ester; it boiled at  $230^\circ$  corr./20 mm., and is a colourless oil.

0.1356 gave 0.3866  $CO_2$  and 0.1438  $H_2O$ .  $C = 77.8$ ;  $H = 11.8$ .

0.1090 „ 0.3112  $CO_2$  „ 0.1168  $H_2O$ .  $C = 77.9$ ;  $H = 11.9$ .

$C_{20}H_{36}O_2$  requires  $C = 77.9$ ;  $H = 11.7$  per cent.

$d_{15}^{16} = 0.9079$ ;  $\alpha_D + 46^\circ$  in a 1 dcm. tube, whence  $[\alpha]_D^{20} + 50.7^\circ$ .

A specimen of this ester was sent to Dr. W. H. Perkin, sen., who very kindly determined its density, magnetic rotation, and refractive power, with the following results:

*Density determinations*:  $d_{10}^{10} 0.91064$ ;  $d_{15}^{15} 0.90741$ ;  $d_{20}^{20} 0.90456$ .

*Magnetic Rotation.*

	<i>l.</i>	<i>t.</i>	Sp. rotation.	Mol. rotation.	Optical rotation.
(1)	175 mm.	13.9°	1.1189	21.065	$[\alpha]_D + 50.69^\circ$
(2)	104 mm.	14.3	1.1115	20.976	$[\alpha]_D + 50.73$

Average molecular rotation, 21.020.

The calculated values on the basis of ethyl stearate,  $C_{20}H_{40}O_2$ , mol. rot. 20.797, (1) with two unsaturated linkings ( $-H_2 \times 2 = +1.112 \times 2$ ); (2) with ring formation ( $-0.6$ ) and a single unsaturated linking ( $-H_2 = +1.112$ ); (3) with ring formation ( $-0.6$ ) and a single allyl group ( $-H_2 = +0.913$ ), are as follows:

	Ethyl Stearate	Mol. rotation.
(1) Two unsaturated linkings ( $-H_2 \times 2 = +1.112 \times 2$ )		20.797
		2.224
		<hr/> 23.021
	Ethyl stearate	20.797
(2) Ring formation ( $-0.6$ )		0.600
		<hr/> 20.197
One unsaturated linking ( $-H_2 = +1.112$ )		1.112
		<hr/> 21.309
	Ethyl stearate	20.797
(3) Ring formation ( $-0.6$ )		0.600
		<hr/> 20.197
One allyl group ( $-H_2 = +0.913$ )		0.913
		<hr/> 21.110

The value found, namely, 21.020, is seen to approximate very closely to the third calculated value, 21.110, which is that for an ester having the formula  $C_{20}H_{36}O_2$ , containing a closed ring and one unsaturated linking of an allylic nature.

*Refractive Power.*

$$d_{15.4^\circ/4^\circ} 0.90637.$$

	$\mu_{15.4^\circ}$	$\frac{\mu-1}{d}$	$\frac{\mu-1}{d}p$
H $\alpha$ .....	1.46000	0.50752	156.315
H $\beta$ .....	1.46851	0.51691	159.208
H $\gamma$ .....	1.47404	0.52300	161.085

$$\text{Dispersion (H}\gamma - \text{H}\alpha) = 4.770.$$

*Chaulmoogramide*,  $C_{17}H_{31} \cdot \text{CO} \cdot \text{NH}_2$ .

The amide was prepared according to Aschan's method (*Ber.*, 1898, 31, 2344), which consists in first converting the acid into its chloride by treating it with phosphorus trichloride, and then pouring the product into well-cooled, concentrated, aqueous ammonia. The white solid thus formed was thoroughly washed with water, dried, and crystallised several times from hot ethyl alcohol. It melted at  $106^\circ$ .

0.1039 gave 0.2942  $\text{CO}_2$  and 0.1112  $\text{H}_2\text{O}$ . C = 77.2; H = 11.9.

$C_{18}H_{33}\text{ON}$  requires C = 77.4; H = 11.8 per cent.

4.3 grams in 100 c.c. of chloroform gave  $\alpha_D + 1.14'$  in a 50 mm. tube, whence  $[\alpha]_D^{27^\circ} + 57.3^\circ$ .

*Ethyl Dibromodihydrochaulmoograte*,  $C_{17}H_{31}\text{Br}_2 \cdot \text{CO}_2\text{Et}$ .

Seventeen grams of ethyl chaulmoograte were dissolved in 50 c.c. of dry chloroform. To this solution, cooled below  $0^\circ$ , a solution of 9 grams of dry bromine in 30 c.c. of dry chloroform was gradually added in the absence of light; the bromine was rapidly absorbed and without any evolution of hydrogen bromide. When all the bromine had been introduced, and after a lapse of several minutes, a permanent redness was apparent. After the removal of the slight excess of bromine by agitation with aqueous sodium hydrogen sulphite, the chloroform solution was washed, first with water, then with dilute aqueous sodium carbonate, again with water, and finally dried with calcium chloride. The chloroform was then removed by aspirating a rapid current of dry air through the liquid, which was maintained at  $25^\circ$ . The product was a nearly colourless oil, and was not markedly

unstable. A portion which had been exposed in a vacuum desiccator over paraffin wax was analysed:

0.3270 gave 0.2546 AgBr. Br = 33.1.

0.2634 „ 0.2050 AgBr. Br = 33.1.

$C_{20}H_{36}O_2Br_2$  requires Br = 34.1 per cent.

*Bromodihydrochaulmoogric Acid,  $C_{17}H_{32}Br \cdot CO_2H$ .*

Chaulmoogric acid (8.5 grams) was gently warmed in 25 c.c of a 68 per cent. solution of hydrogen bromide in glacial acetic acid, the mixture being maintained at 40—50° for about five minutes. On cooling, the liquid formed two layers, and the uppermost, which became solid, was accordingly separated, thoroughly washed with water, and finally dried on a porous plate; it was optically inactive, melted at 36—38°, and was shown by analysis to be bromodihydrochaulmoogric acid.

0.2102 gave 0.1040 AgBr. Br = 21.0

$C_{18}H_{33}O_2Br$  requires Br = 22.2 per cent.

*Action of Sodium and Amyl Alcohol on Chaulmoogric Acid. The Formation of Chaulmoogryl Alcohol,  $C_{18}H_{33} \cdot OH$ , and Chaulmoogryl Chaulmoograte,  $C_{17}H_{31} \cdot CO_2 \cdot C_{18}H_{33}$ .*

Thirty grams of chaulmoogric acid were dissolved in 750 c.c. of amyl alcohol and the solution boiled; six grams of sodium were then introduced, and the liquid vigorously heated until the metal had all dissolved. The solution was then acidified with sulphuric acid, well shaken, and the aqueous acid layer removed. The amyl-alcoholic solution was then washed several times with water, and again vigorously boiled and treated with a further 6 grams of sodium. This entire process was repeated six times. The amyl-alcoholic solution from the last treatment with sodium, after having been acidified with sulphuric acid and subsequently washed with water, was distilled in order to remove the greater part of the amyl alcohol. The remainder of the latter was eliminated by distillation in steam. The residue, which contained a supernatant layer, was extracted with ether, the ethereal solution being washed, dried, and the solvent removed. The product was then fractionally distilled under 18 mm. pressure, when the following fractions were obtained: (1) below 244° (a small amount); (2) 244—254° (15 grams); (3) 254—354° (1—2 grams); (4) 354—358° (5 grams). All these fractions became crystalline on cooling.

*Chaulmoogryl Alcohol*,  $C_{18}H_{33}\cdot OH$ .

*Fraction (1).*—This fraction, which was not entirely soluble in warm aqueous potassium hydroxide, was therefore saponified with the latter, and the undissolved crystalline substance dissolved in ether. The ethereal solution was then extracted several times with concentrated aqueous potassium hydroxide, washed with water, dried, and the solvent removed. The residual, colourless oil soon formed a hard, crystalline cake, which, after recrystallisation, first from acetone and then repeatedly from methyl alcohol, separated in long needles, melting sharply at  $36^{\circ}$ .

0.1016 gave 0.3016  $CO_2$  and 0.1162  $H_2O$ .  $C=81.0$ ;  $H=12.7$ .

0.1246 „ 0.3688  $CO_2$  „ 0.1430  $H_2O$ .  $C=80.7$ ;  $H=12.8$ .

$C_{18}H_{34}O$  requires  $C=81.2$ ;  $H=12.8$  per cent.

5.48 grams in 100 c.c. of chloroform gave  $\alpha_D + 1^{\circ}36'$  in a 50 mm. tube, whence  $[\alpha]_D + 58.4^{\circ}$ .

Chaulmoogryl alcohol is unsaturated, for it readily decolorises a solution of bromine in chloroform.

*Fraction (2).*—This was shown to consist entirely of chaulmoogric acid, no reduction to the dihydro-acid having taken place.

*Chaulmoogryl Chaulmoograte*,  $C_{17}H_{31}\cdot CO_2\cdot C_{18}H_{33}$ .

*Fractions (3) and (4).*—These were combined, dissolved in ether, the solution repeatedly extracted with aqueous potassium hydroxide, then with water, dried, and the solvent removed. The crystalline residue was recrystallised from ethyl acetate, from which it formed small, glistening rosettes, melting at  $42^{\circ}$ .

0.1430 gave 0.4272  $CO_2$  and 0.1572  $H_2O$ .  $C=81.5$ ;  $H=12.2$ .

$C_{36}H_{64}O_2$  requires  $C=81.8$ ;  $H=12.1$  per cent.

This substance was definitely shown to be chaulmoogryl chaulmoograte by the fact that on hydrolysis it afforded on the one hand chaulmoogric acid and on the other chaulmoogryl alcohol, both of which were identified by their properties and by analysis.

*Reduction of Bromodihydrochaulmoogric Acid with Zinc Dust and Alcohol. Formation of Dihydrochaulmoogric Acid*,  $C_{17}H_{33}\cdot CO_2H$ .

To a warm solution of 175 grams of bromodihydrochaulmoogric acid in alcohol, 60 grams of zinc dust were gradually added, and, after the introduction of the whole of the latter, the mixture was heated during

two hours in a reflux apparatus on a water-bath. The alcohol was then removed, the residue, which contained zinc salts, was treated with boiling aqueous potassium hydroxide to decompose the latter, subsequently acidified with sulphuric acid, and the liberated acids extracted with ether, the ethereal solution being washed, dried, and the ether removed. The product was then treated with a 68 per cent. solution of hydrogen bromide in glacial acetic acid, as described on p. 856 for the preparation of bromodihydrochaulmoogric acid. This is necessary in order to reconvert into a bromo-acid the unsaturated acid formed from bromodihydrochaulmoogric acid by the action of the zinc oxide contained in the zinc dust employed. The product from the treatment with hydrogen bromide was then dissolved in alcohol, again subjected to the action of zinc dust, as described above, and this entire operation was repeated six times.

The final product contained a saturated acid in preponderating amount, and, after distillation under diminished pressure, which removed some less volatile condensation product, was crystallised several times from glacial acetic acid saturated with hydrogen bromide. In this way, the last traces of unsaturated acids were eliminated, and the dihydro-acid was obtained in glistening leaflets which, after a final crystallisation from ethyl acetate, melted sharply at  $71-72^{\circ}$ , and this melting point was not altered by further crystallisation.

0.1370 gave 0.3840  $\text{CO}_2$  and 0.1520  $\text{H}_2\text{O}$ .  $\text{C} = 76.4$ ;  $\text{H} = 12.3$ .

0.1000 „ 0.2804  $\text{CO}_2$  „ 0.1098  $\text{H}_2\text{O}$ .  $\text{C} = 76.5$ ;  $\text{H} = 12.2$ .

0.1101 „ 0.3082  $\text{CO}_2$  „ 0.1218  $\text{H}_2\text{O}$ .  $\text{C} = 76.3$ ;  $\text{H} = 12.3$ .

$\text{C}_{18}\text{H}_{34}\text{O}_2$  requires  $\text{C} = 76.6$ ;  $\text{H} = 12.1$  per cent.

Dihydrochaulmoogric acid boils at  $248^{\circ}/20$  mm. and is optically inactive; it is a saturated acid, since permanganate is entirely without action on it, and its solution in chloroform does not decolorise the slightest trace of bromine in the same solvent.

*Methyl Dihydrochaulmoograte*,  $\text{C}_{17}\text{H}_{33} \cdot \text{CO}_2\text{Me}$ .

This ester was readily obtained by dissolving dihydrochaulmoogric acid in methyl alcohol, adding concentrated sulphuric acid, and allowing the reaction to proceed for several hours. The ester, which formed a solid layer on the surface of the cold liquid, was extracted with ether, the ethereal solution being washed successively with aqueous sodium carbonate and water, dried, and the solvent removed. It was then distilled, when it passed over at  $222-223^{\circ}/20$  mm. as a colourless oil, which, on cooling, formed a hard, crystalline mass melting at  $26-27^{\circ}$ .

0.1316 gave 0.3708  $\text{CO}_2$  and 0.1442  $\text{H}_2\text{O}$ .  $\text{C} = 76.8$ ;  $\text{H} = 12.2$ .

0.0904 „ 0.2554  $\text{CO}_2$  „ 0.0994  $\text{H}_2\text{O}$ .  $\text{C} = 77.0$ ;  $\text{H} = 12.2$ .

$\text{C}_{19}\text{H}_{36}\text{O}_2$  requires  $\text{C} = 77.0$ ;  $\text{H} = 12.2$  per cent.

*Action of Hydriodic Acid on Chaulmoogric Acid. Formation of Dihydrochaulmoogric Acid and a Hydrocarbon, Chaulmoogrene.*

Chaulmoogric acid, in quantities of 15 grams for each experiment, was mixed with 20 grams of hydriodic acid (sp. gr. 1.9) and 3 grams of amorphous phosphorus, and the mixture heated in a sealed tube at 200° during three hours. By working up the product in the usual manner, one obtained: (a) a mixture of acids, from which, after much difficulty, a very small amount of dihydrochaulmoogric acid was isolated, and (b) a neutral oil. The acid was analysed:

0.1693 gave 0.4710 CO<sub>2</sub> and 0.1836 H<sub>2</sub>O. C = 75.9; H = 12.0.

0.1013 „ 0.2820 CO<sub>2</sub> „ 0.1114 H<sub>2</sub>O. C = 75.9; H = 12.2.

0.1030 „ 0.2886 CO<sub>2</sub> „ 0.1110 H<sub>2</sub>O. C = 76.4; H = 12.0.

C<sub>18</sub>H<sub>34</sub>O<sub>2</sub> requires C = 76.6; H = 12.1 per cent.

The neutral oil was fractionally distilled under diminished pressure, and, finally, many times over sodium, until the latter remained unchanged; it then passed over at 193—194°/20 mm. as a colourless liquid, which was optically inactive.

0.1353 gave 0.4271 CO<sub>2</sub> and 0.1643 H<sub>2</sub>O. C = 86.1; H = 13.5.

0.0940 „ 0.2980 CO<sub>2</sub> and 0.1170 H<sub>2</sub>O. C = 86.4; H = 13.8.

C<sub>18</sub>H<sub>34</sub> requires C = 86.4; H = 13.6 per cent.

The analyses show that this substance is a hydrocarbon; it is accordingly designated chaulmoogrene.

When it was attempted to fuse chaulmoogric acid with either potassium or sodium hydroxide, no satisfactory result could be obtained, owing to the insolubility of the respective salts of the acid in the fused alkali hydroxides, from which they separated in solid lumps which were not attacked even at 300°.

*Oxidation of Chaulmoogric Acid with Potassium Permanganate (O = 1 atomic equivalent). Formation of Dihydroxydihydrochaulmoogric Acid, C<sub>17</sub>H<sub>31</sub>(OH)<sub>2</sub>•CO<sub>2</sub>H.*

One hundred grams of chaulmoogric acid were dissolved in a solution of 150 grams of potassium hydroxide in 7 litres of water. To this solution, the temperature of which throughout the operation was between 10° and 14°, a dilute solution of 40 grams of potassium permanganate was gradually added. Oxidation took place rapidly, and when all the permanganate had been introduced the mixture was allowed to remain for some time, and the precipitated oxide removed

by filtration. The filtrate was then concentrated and acidified with sulphuric acid, when a white, solid substance separated. This was extracted with ether, the ethereal liquid being washed, dried, and the solvent removed. The solid residue was then extracted with light petroleum, which removed a small amount of unchanged chaulmoogric acid. The portion insoluble in petroleum was crystallised repeatedly from warm benzene, then from acetone, ethyl acetate, and, finally, again from acetone, from which it separated in aggregates of fine needles, melting at  $102^{\circ}$ .

0.1068 gave 0.2680  $\text{CO}_2$  and 0.1042  $\text{H}_2\text{O}$ .  $\text{C} = 68.5$ ;  $\text{H} = 10.8$ .

0.1112 „ 0.2782  $\text{CO}_2$  „ 0.1068  $\text{H}_2\text{O}$ .  $\text{C} = 68.2$ ;  $\text{H} = 10.7$ .

$\text{C}_{18}\text{H}_{34}\text{O}_4$  requires  $\text{C} = 68.8$ ;  $\text{H} = 10.8$  per cent.

*Oxidation of Chaulmoogric Acid with Potassium Permanganate* ( $\text{O} = 4-5$  atomic equivalents). *Formic Acid and Two Dibasic Acids*,  $\text{C}_{17}\text{H}_{30}\text{O}_4$  and  $\text{C}_{17}\text{H}_{30}\text{O}_5$ .

When chaulmoogric acid, dissolved in dilute aqueous potassium hydroxide, was oxidised at the ordinary temperature with an amount of permanganate equivalent to 4—5 atomic proportions of oxygen, the following substances were produced:

(a) Formic acid, which was isolated in the form of its barium salt and the latter analysed.

(b) A mixture of several other acids, which were converted into their ethyl esters. On distilling these under diminished pressure (10 mm.), they yielded the following fractions:

(1)  $210-220^{\circ}$ ; (2)  $220-260^{\circ}$ ; (3)  $260-270^{\circ}$ ; and (4)  $270-280^{\circ}$ , a very small amount.

*Fraction (1).*—This, which became crystalline on cooling, was drained from a little adhering oil and then crystallised from methyl alcohol, from which it separated in shining leaflets, melting at  $26-27^{\circ}$ .

0.0724 gave 0.1882  $\text{CO}_2$  and 0.0710  $\text{H}_2\text{O}$ .  $\text{C} = 70.9$ ;  $\text{H} = 10.9$ .

0.0622 „ 0.1608  $\text{CO}_2$  „ 0.0606  $\text{H}_2\text{O}$ .  $\text{C} = 70.5$ ;  $\text{H} = 10.8$ .

$\text{C}_{21}\text{H}_{38}\text{O}_4$  requires  $\text{C} = 71.2$ ;  $\text{H} = 10.7$  per cent.

0.5140 required  $\text{NaOH}$  equivalent to 29.1 c.c. of a decinormal solution, instead of 29 c.c., the calculated amount for  $\text{C}_{15}\text{H}_{28}(\text{CO}_2\text{Et})_2$ .

A silver salt of the corresponding acid was prepared from the sodium salt.

0.1728 gave 0.0718  $\text{Ag}$ .  $\text{Ag} = 41.6$ .

$\text{C}_{17}\text{H}_{28}\text{O}_4\text{Ag}_2$  requires  $\text{Ag} = 42.3$  per cent.

It was thus shown that the fraction of ester boiling at

210—220°/10 mm. consisted of the diethyl ester of a dibasic acid having the formula  $C_{17}H_{30}O_4$ .

*Fraction (3).*—This slowly deposited a small quantity of a crystalline ester which, when crystallised from light petroleum, separated in needles, melting at 53°.

0.0974 gave 0.2420  $CO_2$  and 0.0884  $H_2O$ .  $C = 67.7$ ;  $H = 10.1$ .

0.0972 „ 0.2416  $CO_2$  „ 0.0892  $H_2O$ .  $C = 67.8$ ;  $H = 10.2$ .

$C_{21}H_{38}O_5$  requires  $C = 68.1$ ;  $H = 10.3$  per cent.

0.3722 required NaOH equivalent to 20.7 c.c. of a decinormal solution, instead of 20.1 c.c., the calculated amount for  $C_{15}H_{28}O(CO_2Et)_2$ .

By the hydrolysis of this ester (m. p. 53°), the corresponding acid was obtained, which, on recrystallisation from ether, formed glistening laminæ, melting at 128°.

0.1200 gave 0.2852  $CO_2$  and 0.1012  $H_2O$ .  $C = 64.8$ ;  $H = 9.4$ .

0.0740 „ 0.1756  $CO_2$  „ 0.0620  $H_2O$ .  $C = 64.6$ ;  $H = 9.3$ .

$C_{17}H_{30}O_5$  requires  $C = 65.0$ ;  $H = 9.5$  per cent.

0.4576 required NaOH equivalent to 29.5 c.c. of a decinormal solution, instead of 29.2 c.c., the calculated amount for a dibasic acid having the formula  $C_{17}H_{30}O_5$ .

The silver salt was prepared from the sodium salt.

0.1982 gave 0.0806 Ag.  $Ag = 40.6$ .

0.0996 „ 0.1412  $CO_2$ , 0.0472  $H_2O$ , and 0.0400 Ag.

$C = 38.6$ ;  $H = 5.3$ ;  $Ag = 40.2$ .

$C_{17}H_{28}O_5Ag_2$  requires  $C = 38.6$ ;  $H = 5.3$ ;  $Ag = 40.8$  per cent.

It was thus proved that this acid is a dibasic acid having the formula  $C_{17}H_{30}O_5$ .

The products of the oxidation of chaulmoogric acid are being further investigated, and will be more fully described and characterised in the next communication on this subject.

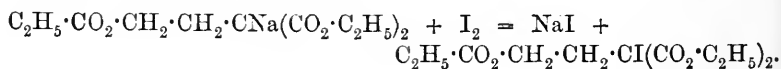
We desire to express our thanks to Mr. F. H. Lees for the valuable aid he has given us throughout this investigation.

THE WELLCOME CHEMICAL RESEARCH LABORATORIES,  
LONDON, E.C.

LXXXVII.—*Studies on Ethyl Carboxyglutarate.*

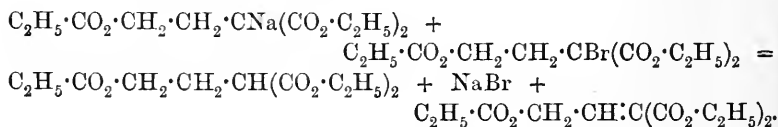
By OSWALD SILBERRAD, Ph.D., and THOMAS HILL  
EASTERFIELD, M.A., Ph.D.

*Action of Halogens on Ethyl Sodiocarboxyglutarate* (compare Proc., 1904, 20, 114).—It has been found by Bischoff and Hausdörfer (*Annalen*, 1887, 239, 110) that when the sodium derivative of ethyl ethylmalonate or ethyl benzylmalonate is treated with iodine, the product formed is not a derivative of ethanetetracarboxylic acid, but a halogen derivative of the alkyl malonate. Ethyl sodiocarboxyglutarate has been found to furnish a further interesting instance of this behaviour. When halogens are allowed to act on ethyl sodiocarboxyglutarate, no condensation occurs, but instead of ethyl carboxydiglutamate, the halogen derivatives of the original ethyl carboxyglutarate are formed. The latter proved to be identical with the compounds obtained by the direct halogenation of ethyl carboxyglutarate, the reaction being thus represented :

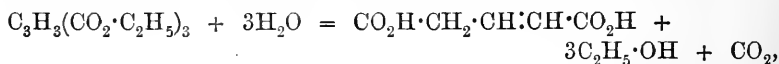


This having been shown to take place for the three halogens, it appeared of interest to ascertain the nature of the reaction between ethyl bromocarboxyglutarate and ethyl sodiocarboxyglutarate.

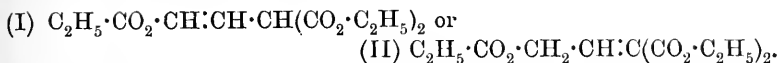
*Action of Ethyl Bromocarboxyglutarate on Ethyl Sodiocarboxyglutarate* (compare Proc., 1904, 20, 141).—On bringing together the halogen and sodium derivatives, they react and give rise to a mixture of the original ethyl carboxyglutarate and a new unsaturated ester,  $\text{C}_{12}\text{H}_{18}\text{O}_6$ . The reaction, which appears to be unlike anything hitherto observed, may be represented as follows :



This unsaturated ester is thus to be regarded as ethyl  $\alpha$ -carboxy- $\Delta^{\alpha\beta}$ -glutaconate. On saponification, it yields a new carboxyglutaconic acid, which readily breaks up into glutaconic acid and carbon dioxide :



from which it will be seen that the constitution of the ester must be represented by one of the following formulæ :



Of these, the former represents ethyl isoitaconate, from which the new ester differs in containing no active hydrogen, as it will not form a sodium derivative.

### EXPERIMENTAL.

(1) *Action of Halogens on Ethyl Sodiocarboxyglutarate.*—Ethyl carboxyglutarate (26.4 grams) (Emery, Ber., 1891, 24, 282) was mixed with 3 grams of finely-divided sodium suspended in 150 c.c. of toluene, and to this mixture 17.5 grams of iodine dissolved in toluene were gradually added, the whole being then warmed for 10 hours on the water-bath. The product was then freed from excess of iodine by means of sodium hydrogen sulphite, washed, dried, and the toluene distilled off on the water-bath, the pressure being finally reduced to 2 mm. The iodo-ester so obtained is a pale amber-coloured, heavy oil, which readily loses iodine.

Found I = 31.60.

*Ethyl α-iodocarboxyglutarate*,  $\text{C}_{12}\text{H}_{19}\text{O}_6\text{I}$ , requires 32.73 per cent.

*Ethyl α-bromocarboxyglutarate* was prepared both as above and also, much more readily, by gradually adding a slight excess of bromine to ethyl carboxyglutarate previously warmed to 40°. In the latter case, bromination occurred with copious evolution of hydrogen bromide, from which the ester was finally freed by being placed over caustic potash in a vacuum desiccator. After washing with sodium hydrogen sulphite in order to remove the last traces of bromine, the compound was obtained as a colourless, highly refractive oil having a sp. gr. 1.325 at 15°/4° and possessing an odour resembling that of the bromo-paraffins.

A specimen prepared from the sodio-ester gave 23.01 Br.

“ “ “ by direct bromination “ 23.53 and 23.55 Br.  
 $\text{C}_{12}\text{H}_{19}\text{O}_6\text{Br}$  requires 23.60 Br per cent.

*Ethyl α-chlorocarboxyglutarate* was obtained in a manner precisely similar to that employed for the bromo-ester, which it closely resembles.

A specimen prepared from the sodio-ester gave 11.72 Cl.

“ “ “ by direct chlorination “ 11.80 Cl.  
 $\text{C}_{12}\text{H}_{19}\text{O}_6\text{Cl}$  requires 11.90 per cent.

(2) *Action of Ethyl Bromocarboxyglutarate on Ethyl Sodiocarboxyglutarate.*—Ethyl α-bromocarboxyglutarate (340 grams) was gradually added to the sodio-ester prepared by mixing 260 grams of ethyl

carboxyglutarate with the calculated quantity of sodium ethoxide dissolved in absolute alcohol; the mixture became warm and sodium bromide was rapidly precipitated, the reaction being completed by warming on the water-bath for an hour. On pouring the product into water, a heavy oil separated, which, after washing with dilute acid and drying over potassium carbonate, was distilled under 15 mm. pressure. The entire quantity passed over between  $163^{\circ}$  and  $180^{\circ}$ , and was ultimately found to consist of almost equal quantities of two compounds, which were separated by systematic fractionation under diminished pressure.

*Ethyl  $\alpha$ -carboxy- $\Delta^{\alpha\beta}$ -glutaconate*,  $C_2H_5 \cdot CO_2 \cdot CH_2 \cdot CH : C(CO_2 \cdot C_2H_5)_2$ , formed the less volatile fraction of the above mixture, and, when pure, was a colourless oil (b. p.  $173-176^{\circ}/15$  mm.) which readily absorbed two atoms of bromine.

Found C = 55.67; H = 7.14.  $C_{12}H_{18}O_6$  requires C = 55.8; H = 7.0 per cent.

The fact that the new ester is not acted on by granulated sodium suspended in toluene is additional evidence in favour of the  $\alpha\beta$ -position for the unsaturated bond.

*Hydrolysis of Ethyl Carboxyglutaconate*.—Ethyl carboxyglutaconate (10 grams) was hydrolysed by boiling with aqueous hydrochloric acid (1:3). The product was freed from hydrochloric acid by evaporation and precipitated in the form of its silver salt; the latter was then suspended in water and decomposed with sulphuretted hydrogen. After concentrating on the water-bath, a syrup was obtained; this, when left in a vacuum desiccator, slowly solidified to a crystalline mass which, after recrystallisation, melted at  $132^{\circ}$  and proved to be glutaconic acid.

Found C = 46.06; H = 4.79.

$C_5H_6O_4$  requires C = 46.6; H = 4.6 per cent.

*Ethyl carboxyglutarate*,  $C_2H_5 \cdot CO_2 \cdot CH_2 \cdot CH_2 \cdot CH(CO_2 \cdot C_2H_5)_2$ , formed the more volatile fraction of the product resulting from the action of ethyl bromocarboxyglutarate on ethyl sodiocarboxyglutarate; it boiled at  $162-163^{\circ}$  (15 mm.).

C = 55.33; H = 7.82.  $C_{12}H_{20}O_6$  requires C = 55.4; H = 7.7 per cent.

The ester was further identified as follows: 25 grams were dissolved in boiling aqueous hydrochloric acid (1:3). The concentrated solution was left in a vacuum desiccator until a syrupy, semi-crystalline mass was obtained, from which glutaric acid was isolated after repeated crystallisation.

LXXXVIII.—*The Nitration Products of the Isomeric Dichlorobenzenes.*

By PERCIVAL HARTLEY and JULIUS BEREND COHEN.

THE progressive nitration of the dichlorotoluenes has been investigated by Cohen and Dakin (Trans., 1902, 81, 1344), and the constitution of the mono- and di-nitro-derivatives has been ascertained in each case. The results show that the two nitro-groups in the dinitro-derivatives of the 6-dichlorotoluenes follow strictly the meta-law of substitution.

Since the publication of this communication, three papers on the nitration products of *o*-, *m*-, and *p*-dichlorobenzene have appeared. Morgan (Trans., 1902, 81, 1378), who studied the nitration of the para-compound and confirmed the observation of Jungfleisch (*Jahresber.*, 1868, 343) that two dinitro-compounds are formed, states that "the nitration product consists chiefly of the isomeric 2:5-dinitro-1:4-dichlorobenzene, the required 2:6-dinitro-1:4-dichlorobenzene being only a by-product. This result is of interest, because it affords another illustration of the fact that, as substitution progresses, the rules governing the orientation of entrant radicles become considerably modified."

The second paper is by Blanksma and Terwogt (*Rec. trav. chim.*, 1902, 21, 286) on the derivatives of 1:3-dichloro-4:6-dinitrobenzene, the position 6 allotted to the second nitro-group being apparently based on Nietzki and Kehrman's observations (*Ber.*, 1887, 20, 334).

In the third paper, Blanksma (*Rec. trav. chim.*, 1902, 21, 419) deals with the products of the nitration of *o*-dichlorobenzene, and states that on nitrating *o*-dichlorobenzene only a little 1:2:4:6-dichloro-dinitrobenzene is obtained, the 1:2:4:5-isomeride being formed in greater proportion.

No quantities are given, and no proof is offered that the principal product is an ortho-dinitro-compound.

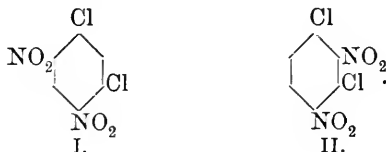
If the above facts are correct, the principal products of nitration are an ortho-dinitro-compound in the case of *o*-dichlorobenzene, a meta-dinitro-compound in the case of *m*-dichlorobenzene, and a para-dinitro-compound in the case of the para-isomeride.

On the other hand, there is an absence of data of both a qualitative and quantitative character in regard to the ortho- and para-compounds, without which any important departure from the meta-law of substitution by the entrant nitro-groups cannot be regarded as being established. We have therefore repeated the nitration of the three

dichlorobenzenes in order to obtain the required information. Before studying the dinitro-compounds, we have ascertained the position occupied by the first nitro-group in each of the three cases. The results of further nitration may be briefly summarised as follows :

The conversion of *o*-dichlorobenzene into a dinitro-compound is peculiarly difficult to effect, and after heating it at 110—120° with a large excess of fuming nitric acid mixed with double its weight of fuming sulphuric acid for 32 hours, only about 25 per cent. of the theoretical amount of the dinitro-compound (m. p. 104°) was obtained, the remainder of the product being mononitro-compound. This substance is an ortho-dinitro-compound, and the formula given by Blanksma is therefore correct.

*m*-Dichlorobenzene is wholly converted into a meta-dinitro-derivative, which, according to Nietzki and Kehrman (*loc. cit.*), has the first of the two alternative formulæ :



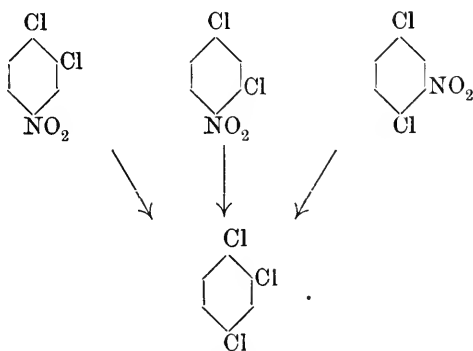
*p*-Dichlorobenzene gives two dinitro-derivatives, the meta- and para-compounds, as stated by Morgan, but we find the yield of meta-compound to be about 6 times that of the para-isomeride.

Hence, the only notable divergence from the meta-law is exhibited by *o*-dichlorobenzene. Both the resistance offered to the introduction of the second nitro-group and the position eventually occupied by it, afford a curious exception to the ordinary rule for which it is difficult to find an explanation.

#### EXPERIMENTAL.

##### *Constitution of the Mononitro-derivatives of the Dichlorobenzenes.*

The method of determining the constitution of the three mononitro-derivatives obtained by nitrating the three dichlorobenzenes was to replace the nitro-group by chlorine in the usual way. Each of the compounds gave the same trichlorobenzene, which formed a trichloronitrobenzene (m. p. 57—58°), the latter being converted into a tetrachlorobenzene (m. p. 138—139°). The mononitro-derivatives must therefore have the following formulæ :



Trichlorobenzene.  
(Nitrocompound m. p. 57—58°).

*Nitration of o-Dichlorobenzene.*

To 10 grams of the *o*-dichlorobenzene prepared from *o*-chloronitrobenzene (Kahlbaum) was slowly added a cold mixture of 40 grams of fuming nitric acid (sp. gr. 1.5) and 75 grams of fuming sulphuric acid containing 18 per cent. of  $\text{SO}_3$ . The mixture was then heated on the oil-bath for 16 hours at 110—120°; the product, which was poured into water and left until the insoluble portion became hard, was then filtered, powdered, dried, and treated with the same quantity of acids, and for the same length of time as before. The final product was recrystallised from acetic acid and water, and yielded about a fourth of its weight of colourless, foliated crystals melting at 104°. The remainder from its low melting point (it is semi-solid at the ordinary temperature) appeared to consist mainly of unaltered mononitro-compound (m. p. 43°).

Blanksma's method consists in heating the dichlorobenzene with a mixture of 4 times its weight of fuming nitric acid and 6 times its weight of concentrated sulphuric acid for one hour on the water-bath, and he obtained a product melting at 110°. We cannot confirm his results, for in some preliminary experiments carried out in a similar manner with the addition of a stirring apparatus to keep the acid and dichlorobenzene well mixed, the product did not solidify after heating on the water-bath for a week.

The compound melting at 104° was reduced to the diamine with tin and hydrochloric acid; this base gave the phenanthraquinone test for ortho-diamines, but no reaction with nitrous acid, thus showing the absence of a meta-diamine. The original compound must therefore be 1:2-dichloro-4:5-dinitrobenzene.

*Nitration of m-Dichlorobenzene.*

The *m*-dichlorobenzene prepared from *m*-nitroaniline was nitrated in the manner described in the case of the *o*-compound, the mixture being heated for 8 hours at 110—120° and then poured into water. A theoretical yield of crude dinitro-compound (m. p. 80—90°) was obtained (the mononitro-compound melts at 33°). After one crystallisation from alcohol it melted at 99—100°, and at 103° after a second crystallisation. Fifty to sixty per cent. of the pure substance was thus obtained. No other product could be isolated from the mother liquor, and the absence of any ortho-dinitro-compound, which is the only other possible product, was assured by reducing the crude dinitro-compound and applying the phenanthraquinone test. A second nitro-group occupying a meta-position to the first leaves a choice between two formulæ, as already stated. We attempted to confirm Nietzki and Kehrmann's formula by nitrating 1:3-dichloro-2-nitrobenzene, which can only give formula II on p. 866, but have not yet obtained this substance in a pure state.

*Nitration of p-Dichlorobenzene.*

The nitration of *p*-dichlorobenzene was conducted in two steps. The pure mononitro-compound (m. p. 54°) was first prepared and then treated as described by Morgan (*loc. cit.*). The product, which slowly solidified when poured into water, was filtered and dried, the treatment with acid being repeated to ensure complete nitration. An attempt was made to separate the two dinitro-derivatives by fractional crystallisation from alcohol, but although the pure dinitro-compounds were eventually obtained, the process proved to be useless as a quantitative method of separation. The meta-dinitro-compound crystallises from alcohol in large, colourless plates (m. p. 101—102°) (Engelhardt and Latschinow, *Zeitsch. für Chemie*, 1870, 234, give 101°). The para-compound crystallises in long prisms which melt at 105—106° (E. and L. give 104°). The positions of the nitro-groups were confirmed by reduction and the application of the usual tests for diamines.

The quantitative method which we have employed for estimating the two dinitro-compounds in the mixture is to reduce them to the diamines, as described by Morgan, but, instead of using water, the separation of the bases was effected by means of alcohol, in which the para-compound is very slightly soluble. Tin and hydrochloric acid were used for reduction as giving a cleaner product than the iron and hydrochloric acid employed by Morgan. The reduction product

was made alkaline and at once extracted with chloroform. After dehydrating and removing the chloroform, the bases crystallised usually with a red tint, which became deeper the longer the product was exposed to the air. As the quantitative estimation of the original dinitro-compounds depends in the first instance on a quantitative yield of diamine, the reduction product was weighed in each case and a yield of 88, 90, and 95 per cent. respectively of the theoretical quantity was obtained in 3 experiments with 5, 15, and 20 grams of material. The reduction product was extracted with a small quantity of warm alcohol and filtered from the undissolved portion. The crystals which separated from the mother liquor on cooling were also removed by filtration. Both these portions consist of nearly pure para-diamine, which melts at  $164^{\circ}$ . The mother liquor was then evaporated, the various fractions weighed, and the melting points ascertained. The melting point of the pure meta-diamine is given as  $99-100^{\circ}$ .

The following are the results of 3 experiments :

Weight of the mixed bases.	Less soluble fraction.	M. p.	More soluble fraction.	M. p.	Per cent.	
					Less sol. fraction.	More sol. fraction.
(1) 10 grams	1.1 grams 0.3 „ — 1.4 „	161— $163^{\circ}$ 159—161 —	4.3 grams 1.2 „ 2.5 „ 8.0 „	85— $89^{\circ}$ 75—80 68—72	14	81
(2) 8 „	0.8 „ 0.15 „ — — 0.95 „	162 161—162 — —	1.4 „ 0.6 „ 2.8 „ 1.5 „ 6.3 „	85—90 70—75 70—75 64—70	12	79
(3) 8 „	1.1 „	163	not estimated	—	13.7	—

The results are fairly concordant. In the 3 experiments, 14, 13.7, and 12 per cent. of the mixed bases consist of nearly pure para-compound. It was thought at first that the low melting point of the more soluble portion might be due to the presence of a small amount of the para-compound or of dichloroaniline obtained from dichloronitrobenzene in the crude dinitro-product, but we found that even the most fusible fraction could be easily purified by removing a small

quantity of resinous matter which appears to be formed by the atmospheric oxidation of the base and is insoluble in water.

All the fractions may be purified with very little loss by either distilling in steam, crystallising from hot water, or dissolving in hydrochloric acid, filtering from impurities, and reprecipitating the base.

In conclusion, we wish to thank Mr. R. Barton for his help in conducting some of the preliminary experiments.

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### LXXXIX.—*The Fermentation of the Indigo-plant.*

By CYRIL BERGTHEIL.

THE fermentation which takes place when the indigo-plant is steeped in water in order to extract the dye has been the subject of several investigations, of which the following appear to be the most important.

In 1887, Alvarez described an organism under the name *Bacillus indigogenus*, which he isolated from an infusion of indigo-plant, and to which he ascribed the power of producing the fermentation (*Compt. rend.*, 1887, 115, 286).

In 1896, C. J. van Lookeren and P. J. van der Veen expressed the opinion that the fermentation was due to an enzyme and not to a bacterium; but they neither succeeded in separating the enzyme nor in satisfactorily demonstrating its existence (*Landw. Versuchs-Stat.*, 1896, 46, 249—288).

In 1898, Bréaudat, working with *Isatis alpina*, supported the latter view, and brought evidence to show that the production of indigo from that plant was due to the action of a hydrolysing enzyme on a glucoside contained in the plant. He also concluded that the oxidation of the substance produced by the hydrolytic cleavage of the glucoside, by which indigo is obtained, was brought about under the influence of an oxidase (*Compt. rend.*, 1898, 127, 769).

In view of the important bearing of a thorough understanding of the fermentation process on the manufacture of indigo, it became necessary to re-examine the matter in some detail, and the work now described was carried out in India during the years 1902—1903 with that end in view.

Two specimens of *Indigofera* were used for the investigation—the

plant commonly grown in Bihar for indigo manufacture, and known until lately as *Ind. tinctoria*, but now classified by Prain as *Ind. Sumatrana*, and the Java or Natal variety, *Ind. erecta*. The former cannot be satisfactorily grown in Bihar during the cold weather, and the latter was therefore used. The two species were found to behave in exactly the same manner in all the comparisons made, the only difference being that more indigotin per unit weight of leaf can be obtained from *Ind. erecta* than from the ordinary plant. Only the leaves of the plant were used, since it is well known that practically no indigotin is obtainable from the stems or other parts.

On infusing the leaves in water at temperatures below 80°, the latter acquires a yellow colour with a green fluorescence, the time taken for this to set in varying with the temperature of the water used; simultaneously with the appearance of this colour, the infusion is found capable of giving a precipitate of indigo on being agitated with air. If the extract is made in boiling water, a clear solution is obtained, varying with concentration from light yellow to dark reddish-brown, which is incapable of giving indigo by agitation with air, but does so by the combined action of an acid and an oxidising agent. It is clear, therefore, that a different substance is extracted in the two cases, and it seemed probable that the substance obtained in the former case was derived from that obtained in the latter by fermentation.

Since the extract capable of giving indigo by agitation with air is obtained when the plant is infused in hot water and also in the presence of antiseptics, it seemed exceedingly improbable that the fermentation could depend on bacterial action. Nevertheless, the matter was first investigated from a bacteriological point of view, since it was found that the steeping vat was undoubtedly characterised by great bacterial activity, and many planters were of the opinion that bacterial action was essential to indigo production.

### *Bacteriological Investigation.*

A sterile extract of the indigo-plant was made as follows. Forty grams of leaves were thrown into about 10 times their weight of briskly boiling water, and after boiling for 2—3 minutes the leaves were strained off, the extract poured into sterile test-tubes, and heated in an autoclave at 120° for three-quarters of an hour. After cooling, the tubes were kept at 32° for 24 hours and a subculture then made from one of them into a sterile tube containing nutrient broth, which was incubated at 32° for 24 hours. The broth remained perfectly bright and clear, and microscopic examination of a film prepared from it showed no micro-organisms. The extract of the indigo-plant was therefore sterile. The extract became somewhat darker after sterilisation and

a slight brown precipitate formed; it could, however, be kept for several months in tubes plugged with cotton-wool without undergoing any further alteration, and was found to retain the power of giving indigo by the combined action of an acid and an oxidising agent. It was observed that a tube left exposed to the air gradually assumed the yellowish-green fluorescence characteristic of the fermented extract, and acquired the power of forming indigo on agitation with air. This points to the existence of aerial organisms capable of producing the fermentation, and a microscopic examination of a film from a tube thus exposed was found to show the presence of bacteria of all descriptions. No organism having the specific property of producing indigo fermentation was, however, isolated from such a tube.

Forty grams of indigo leaves were completely steeped in water at about 30° and left for 12 hours. At the end of this time, the infusion was found to have assumed the characteristic greenish-yellow colour and to give copious indigo on atmospheric oxidation. A microscopic examination of a hanging drop from this infusion showed it to contain numerous kinds of bacteria in great quantity, and a film prepared from the same infusion showed many varieties of organisms, but a short bacillus with rounded ends, occurring frequently in pairs and in short chains surrounded by a capsule, seemed to predominate. A subculture was made from this infusion into one of the tubes of sterile indigo extract and incubated at 32°. After 20 hours, the colour of the extract in this tube had changed to yellowish-green and a scum of indigo had formed on the surface. A microscopic examination of a film from this tube showed similar organisms to that from the infusion with which it had been seeded.

It was thus shown that it is possible to set up fermentation in a sterilised extract of the indigo-plant by a very small amount of liquid transferred from an infusion of the plant in cold water. It was, however, possible that a small amount of an enzyme had been transferred to the sterile extract in the drop from the fermenting infusion, and that the bacteria were playing no essential part. To obviate this possibility, a subculture was made from a fermenting infusion into broth. The broth tube was incubated at 32° for 24 hours, after which it was very turbid; a subculture was then made into a second broth tube, which was incubated in its turn. Nutrient agar-agar plates were now made from this culture. Three distinct types of colonies were obtained, but semi-transparent surface colonies with a moist appearance and outline varying from circular to amœboid forms predominated. Microscopic examination of films from these moist colonies showed them to consist of the bacillus previously observed as predominating in infusions of indigo-plant. Subcultures were made from two of these colonies and from one of each of the other two

distinct types of colonies into sterile tubes of indigo extract which were incubated at 32° for 48 hours. None of them acquired the power of forming indigo by atmospheric oxidation. It seemed, therefore, that the fermentation produced in a sterile tube of extract when seeded direct from a fermenting infusion was due to a small amount of enzyme transferred, and not to micro-organisms.

It was thought possible, however, that organisms capable of producing the fermentation in the original infusion lost their power of so doing by prolonged culture in artificial media. To test this point nutrient agar-agar plates were made directly from an indigo infusion. Colonies of the same bacterium as that previously observed were again found to predominate, and on seeding from one of these directly into indigo extract, fermentation was found to have set up after 8 hours' incubation. Tubes of extract seeded from three other types of colony, which were found on microscopic examination to consist of organisms other than the predominant one, also showed slight fermentation after 14 hours. It was impossible that any of these fermentations could be caused by transferred enzyme, since only a minute portion of the growth from the surface of the colonies was taken in each case. On making repeated subcultures from a tube infected in the foregoing manner through a series of fresh tubes of extract, fermentation was always found to take place.

It is clear, therefore, that at least one organism capable of producing indigo fermentation is invariably found in large quantities in an infusion of the plant, and that it loses its power of so doing by continued culture in artificial media. The organism is a bacillus corresponding very closely with the description given by Alvarez of his *Bacillus indigogenus*, and is no doubt identical with it. It is probable that several bacteria occurring in indigo infusions are capable of producing the fermentation, and, from the fact that fermentation may be set up spontaneously in a sterile extract exposed to air, it is clear that there are also aerial organisms capable of doing so.

### *The Indigo Enzyme.*

It was evident from the commencement of the investigation that the indigo fermentation could not be explained by bacterial action alone. The fact of its taking place in the presence of antiseptics strong enough to destroy bacterial life, and at a temperature equally destructive thereof, militated strongly against such an assumption, whilst the fact that the fermentation took place much more rapidly at a high temperature than at a low one seemed to indicate so strongly the presence of an enzyme that further bacteriological investigation

was abandoned, and attempts were made to prove the presence of an unorganised ferment.

A quantity of indigo leaves was reduced to pulp in a mortar, covered with water containing a little chloroform, and left in the incubator at 32° for 12 hours. At the end of this time, a scum of indigo had formed on the surface of the liquid. The pulp was squeezed through cloth and the turbid green liquid thus obtained was divided into two parts. The first part was treated with an equal volume of alcohol (sp. gr. 0.810), which produced a greenish-blue, flocculent precipitate and left the liquid clear and reddish-brown. The precipitate (ppt. A) was collected, washed with dilute alcohol, and transferred to a volume of water slightly less than half that originally taken for extraction; the mixture was shaken vigorously for an hour and then filtered, a clear yellow solution being thus obtained (sol. A). The filtrate from ppt. A was again treated with an equal volume of alcohol; this produced a white, gelatinous precipitate (ppt. B), which was collected and treated in a similar manner to ppt. A, giving a light yellow solution (sol. B). The second part of the original infusion was heated at 60—70° for an hour, when the greater part of the proteids present were thus coagulated and settled out as a heavy, gelatinous precipitate (ppt. C), leaving a clear reddish-brown liquid. The precipitate was collected, shaken up with water as before, and filtered, giving a yellow solution (sol. C). The filtrate from ppt. C was treated with an equal volume of alcohol, which produced a white, gelatinous precipitate (ppt. D). This was filtered off and treated in the same way as the previous precipitates, giving a light yellow solution (sol. D).

The fermentative power of the solutions so obtained was tested on an extract of indigo-plant prepared in the manner described in the bacteriological portion of this paper, except that the sterilisation in the autoclave was dispensed with, the extract being boiled for about ten minutes after straining from the leaves in order to destroy any possible enzyme or bacteria present, and used as soon as it was cold. Five c.c. of such an extract were poured into each of four test-tubes, and the same volume of one of the solutions to be tested was added to each. A fifth tube was prepared containing 5 c.c. of extract and 5 c.c. of water previously boiled and cooled. All were kept at 32° for 12 hours, at the end of which time the tube containing sol. A was strongly fermented and gave a large amount of indigo on shaking up with air. The other tubes were quite unaltered. The same experiments were now repeated, keeping the tubes at 40—50°; at this temperature, the change from brown to greenish-yellow took place in the case of sol. A in a very few minutes, and after an hour fermentation was far advanced. The remaining solutions had produced no perceptible change in the extract. It was found that if the sol. A

were boiled before being added to the extract it entirely lost its power of fermenting the latter.

It was evident, therefore, that there is a substance contained in the leaf of the indigo-plant which is soluble in cold water and can produce the indigo fermentation. Further, that this substance is precipitated on the addition of about 45 per cent. of alcohol to its aqueous solution, and is destroyed by heating at  $100^{\circ}$  in the presence of water; it also appears to be destroyed, or so far coagulated as to be insoluble in water, by heating its aqueous solution at  $70^{\circ}$ . It is apparently as much proteid in nature as the enzymes hitherto investigated, and, by reason of its power of producing fermentative change in the indigo complex occurring in the plant, should be classed among these substances.

The course of the action of this enzymic fermentation was studied in some detail, not only because it might possibly lead to improvements in the method of steeping used in indigo manufacture, but also because it had some theoretical interest. The change taking place under the influence of the enzyme is referred to in this paper as the "fermentation" for lack of a general term to distinguish enzyme action from fermentation under the influence of living organisms.

In the first place, attempts were made to obtain the enzyme in a more active form than in the foregoing sol. A. A dirty-white substance almost entirely soluble in water was obtained from this solution by precipitating with an equal volume of alcohol and drying the precipitate over sulphuric acid under diminished pressure. The solution was made up to the same volume as that from which the precipitate had been derived, and the comparative strengths of the solution thus obtained and of the original solution were determined by adding 5 c.c. of each to 5 c.c. of plant extract and keeping both at  $40-50^{\circ}$ . It was found that the colour change indicating the beginning of fermentation occurred much sooner in the case of the original solution than in that of the solution obtained by redissolving the precipitate. The enzyme, therefore, loses strength by the latter process. A second attempt to obtain a more active product was made by forming a precipitate of calcium phosphate in sol. A by adding a dilute solution of sodium phosphate followed by a solution of calcium chloride, and drying the precipitate over sulphuric acid under diminished pressure. The substance so obtained was extracted with water and the activity of the extract tested as described above; it was found to be considerably less than that of the original sol. A. It seemed, therefore, that the enzyme could not be obtained in a more active form than in sol. A by a process of reprecipitation, and it was ultimately decided to work with sol. A without attempting any process of purification. Such a solution of enzyme was accordingly used in all the earlier experiments, and was

found to be perfectly satisfactory so long as the tests were carried out on small quantities of extract, and colorimetric comparisons depended on to obtain the various data. However, in experiments in which larger quantities of extract were used and the indigotin obtained estimated volumetrically, it was found to be too weak to give sufficient indigotin for estimation in a reasonable period of time. It seemed probable that the enzyme was difficult of extraction owing to the presence of tannin in the leaves. This difficulty has been encountered by several investigators who have worked on enzymes occurring in foliage leaves; notably by Brown and Morris in dealing with diastase (*Trans.*, 1893, 63, 604), and more recently by Mann, working on an enzyme occurring in the tea-leaf ("The Ferment of the Tea-leaf," 1901, and *Abstr.*, 1903, ii, 388). Mann found that by pounding the leaves with hide-powder the tannin was fixed, and the enzyme could then be easily extracted in water.

This method was tried with indigo-leaves and gave very gratifying results, the solution obtained when the leaves were pounded with hide-powder before extraction being very much more active than that obtained when this substance was not used. Accordingly, in all the later experiments the enzyme solution was prepared as follows: the leaves were pounded to a pulp, the pulp mixed intimately with about a third of its weight of hide-powder, and the mass extracted with sufficient water containing a little chloroform to cover it for 12 hours. At the end of this time, the liquid was squeezed out of the pulp through cloth, and the enzyme precipitated with an equal volume of alcohol (sp. gr. 0.810). The precipitate was collected, washed with dilute alcohol, and transferred to a mixture of chloroform and water, with which it was shaken vigorously for an hour, allowed to remain for some hours, again thoroughly agitated, and finally filtered. A very active solution of enzyme could be obtained in this manner, and it was found that by adding a few drops of chloroform such a solution could be kept for several weeks without perceptibly losing strength.

Several attempts were made to obtain the substance yielding indigo, as it occurs in the plant, in a state of purity. This substance would seem to be extracted by steeping the plant in boiling water, since the extract on fermentation gives a solution having the same properties as that obtained by fermenting the plant direct by steeping it in cold water. The extract made in boiling water has only a slight action on Fehling's solution or phenylhydrazine, but the precipitation of indigotin from the extract, either by fermentation and atmospheric oxidation or by the action of an acid and an oxidising agent, is invariably accompanied by the production of a sugar, the presence of which in the solution may be shown by its reducing action on Fehling's solution and its power of forming an osazone with phenylhydrazine. The action

of an acid alone also leads to the production of a reducing sugar, although, in the absence of an oxidising agent, only a small quantity of indigotin is precipitated.

This indicates the derivation of indigotin from a glucoside, but numerous attempts to obtain a pure substance from the extract in boiling water all resulted in failure. The substance occurring in the plants dealt with appears to be much more stable than indican under the influence of heat (compare Schunck, *Mem. Manchester Phil. Soc.*, 1855, 12, 177), since the hot water extract can be evaporated to a sticky, resinous consistency, and the residue dissolved in water repeatedly, without the solution losing its properties of giving indigotin either by fermentation or by the action of an acid and an oxidising agent. Indican, as described by Schunck, is very unstable under these conditions and would entirely decompose. It appears to be impossible, however, to obtain crystalline indican from the extract in the manner described by Hoogerwerf and ter Muelen (*Proc. K. Akad. Wetensch. Amsterdam*, 1900, 2, 520). It was eventually decided to carry on fermentation experiments with the crude extract of the plant in boiling water. This course also had the advantage that the fermentations were carried on under conditions more nearly resembling those which obtain in the steeping-vat used in manufacture than if a purified product were employed.

*Comparison of the Quantity of Indigotin obtained from an Extract of the Plant by the Action of an Acid and an Oxidising Agent, and that obtained by Fermentation.*

With the view of estimating the total amount of indigotin obtainable from an extract of the plant by fermentation, it seemed advisable to ascertain whether the amount corresponded with that obtained from the same extract by the action of an acid and an oxidising agent, since, if an agreement could be shown to exist, the latter would provide a much more rapid method of arriving at the required result than that of carrying the fermentation to a conclusion and determining the indigotin after oxidation with air.

The best method for precipitating indigotin from an extract of the plant is that devised by C. Rawson in 1901 for the analysis of indigo-yielding plants. The extract is made strongly acid with hydrochloric acid, and a solution of ammonium persulphate is gradually added; the indigotin is precipitated in a finely crystalline form, and may be quantitatively estimated by collecting in an asbestos filter, washing the precipitate with boiling water, and, after thoroughly drying the filter with its adherent precipitate at a temperature not exceeding 70°, dissolving the precipitate in concentrated sulphuric acid. The solution

of indigotindisulphonic acid thus obtained is then diluted, cleared by the addition of barium chloride, and a known volume titrated with a standard permanganate solution in the manner described by Rawson (*J. Soc. Dyers and Colourists*, 1885, 1, 74; *J. Soc. Chem. Ind.*, 1899, 18, 251). This method of precipitating and estimating indigotin from an extract was frequently used in the course of the work, and will be referred to as the "persulphuric acid method."

The following method was employed for estimating the total indigotin obtainable from an extract by fermentation. The extract was made in boiling water in the manner already described, and, after boiling thoroughly for some minutes, was allowed to cool in a flask plugged with cotton-wool. About 5 oz. of leaves were used to a litre of water, and these relative quantities were adhered to throughout the investigation. A fresh extract was made for each set of determinations, since it was found that there was always a risk of premature fermentation being set up by aerial organisms when once the flask containing the extract had been unplugged.

Known volumes of the cold extract and an enzyme solution were mixed, the quantities of each being varied according to the number of determinations to be made and the activity of the enzyme solution used. The mixture was allowed to remain in a flask plugged with cotton-wool at the temperature of the air, and a small sample was taken out from time to time and the progress of the action checked by adding a drop of dilute ammonia; this reagent stopped further fermentation, and also considerably accelerated subsequent oxidation. Complete precipitation of all the indigotin obtainable by atmospheric oxidation was insured by shaking the test-tube containing the sample for five minutes. The precipitate was filtered off, the clear yellow filtrate was made acid with hydrochloric acid, and a few drops of ammonium persulphate solution were added, which precipitated the indigotin from the unfermented extract, producing a coloration varying from deep blue to pale green if the action was not finished, whilst the solution remained a clear yellow if fermentation was complete. No difficulty was experienced in bringing the action to completion in a reasonable period of time, providing that sufficient enzyme was added.

When the above test showed that fermentation was complete, one or more samples of known volume were taken from the fermented extract and, after adding a few drops of ammonia, were oxidised by shaking violently for ten minutes or so, the vessel containing the sample being opened from time to time to admit a fresh supply of air. The solution was then rendered strongly acid, boiled, and the precipitate collected on asbestos and the indigotin estimated in the same way as in the persulphuric acid method.

The following are details of the experiments the results of which,

expressed in indigotin obtained from 100 c.c. of extract, are summarised in the annexed table.

*Experiment A.*—The quantity of indigotin obtainable from two portions of extract of 100 c.c. each was determined by the persulphuric acid method (I and II); 220 c.c. of the same extract were fermented with 330 c.c. of a dilute enzyme solution, and fermentation being complete after 6 hours, two portions of 250 c.c. each were withdrawn, oxidised, and the indigotin estimated (III and IV).

*Experiment B.*—The indigotin obtainable from two portions of extract of 100 c.c. each was estimated by the persulphuric acid method (I and II); 325 c.c. of the same extract were fermented with 325 c.c. of an active enzyme solution and fermentation was complete in 1 hour. Two portions of 200 c.c. each were then withdrawn, oxidised, and the indigotin estimated (III and IV). The remainder of the fermented extract was then allowed to remain, and a third portion of 200 c.c. withdrawn after 20 hours from the start. This was oxidised and the indigotin determined as before (V).

*Experiment C.*—The indigotin from 180 c.c. of extract was determined by the persulphuric acid method (I); 900 c.c. of the same extract were fermented with 100 c.c. of enzyme solution and, after 20 hours, fermentation was complete. A portion of 200 c.c. was withdrawn, oxidised, and indigotin determined (II). The remainder was allowed to remain, and after 36 hours from the start a third portion of 200 c.c. was withdrawn, the indigotin obtained by oxidation being then estimated.

	Persulphuric acid method.	Fermentation.
<i>Experiment A...</i>	I. 0·0840 gram.	III. 0·1016 gram.
	II. 0·0847 „	IV. 0·1008 „
<i>Experiment B...</i>	I. 0·044 „	III. 0·0697 „
	II. 0·0427 „	IV. 0·0690 „
		V. 0·0292 „
<i>Experiment C...</i>	I. 0·079 „	II. 0·096 „
		III. 0·0547 „

Thus there is invariably more indigotin obtained by fermentation than by chemical precipitation, so that a measure of the total amount of indigotin obtainable from an extract by fermentation cannot be arrived at in the latter manner.

It is to be noted, by a comparison of the figures obtained in No. V of Experiment B with Nos. III and IV of the same experiment, that a decrease in the amount of indigotin obtainable by atmospheric oxidation takes place if the fermented solution is allowed to remain after fermentation is complete. The same fact is illustrated by a com-

parison of Nos. III and II of Experiment C. The substance produced by fermentation seems to be unstable and to undergo some slow change whereby it loses the power of forming indigotin on oxidation. The fact that a loss of indigotin occurs if the plant is steeped too long in the manufacture is doubtless due to this circumstance.

*The Progress of the Action with Time.*

It has been shown by Adrian Brown in the case of invertase (Trans., 1902, 81, 273), and by Horace Brown and Glendinning in the case of diastase (Trans., 1902, 81, 388), that in solutions fermenting under the action of these enzymes a direct proportionality exists between the duration of the action and the quantity of fermentable substance transformed until a certain stage in the course of the action is reached, after which the proportionality ceases to hold.

It seemed of interest to ascertain whether such a proportionality could be found to exist in the course of the fermentation under consideration, and, if so, at what stage of the action it ceased.

As a preliminary to these and some of the succeeding experiments, it was necessary to show that boiling the indigo extract in the presence of dilute ammonia did not lead to the formation of indigotin or any substance insoluble in boiling water which would decolorise permanganate, and so introduce an error into the estimation of indigotin. An extract (200 c.c.) when boiled for an hour with 1 c.c. of dilute ammonia deepened in colour, but gave neither indigotin nor other precipitate.

Accordingly, the following method was pursued. A known volume of enzyme solution was added to a known volume of the plant extract and the mixture allowed to remain in a flask plugged with cotton-wool at about 30°, and samples of known volume were withdrawn from the flask at equal intervals of time, the amount being decreased as fermentation progressed, since in the more advanced stages sufficient indigotin for an accurate estimation could be obtained from a smaller sample than in the earlier stages. After adding 1 c.c. of dilute ammonia, the samples were oxidised with air, boiled, and the precipitate collected on asbestos, washed with boiling water, and the indigotin estimated as before.

The total amount of indigotin obtainable from the extract by fermentation was determined in a separate portion in the manner described under the last heading.

*Experiment A.*—A little more than 1800 c.c. of extract was fermented with 200 c.c. of enzyme solution. Samples were withdrawn at successive intervals of 45 minutes, the volumes taken being as follows: I. 500 c.c., II. 400 c.c., III. 300 c.c., IV. 300 c.c., V. 200 c.c.,

VI. 200 c.c. Ammonia was added, the sample oxidised, and the indigotin determined; 100 c.c. of extract were fermented separately to give the total indigotin obtainable.

*Experiment B.*—Nine hundred c.c. of extract were fermented with 150 c.c. of enzyme solution. The first sample was withdrawn after  $3\frac{1}{2}$  hours and subsequent samples at intervals of one hour, the volumes taken being as follows: I. 300 c.c., II. 300 c.c., III. 200 c.c., IV. 200 c.c.; 100 c.c. of extract were fermented separately to determine the total indigotin obtainable.

The results of the preceding experiments are summarised in the following table:

Grams of indigotin obtained from 100 c.c. of extract.

No. of sample.....	I.	II.	III.	IV.	V.	VI.	Total obtainable.
<i>Experiment A.</i> ...	0.006	0.0104	0.015	0.0197	0.0235	0.0256	0.1175
Differences .....		0.0044	0.0046	0.0047	0.0038	0.0021	
<i>Experiment B.</i> ...	0.0105	0.014	0.0175	0.0192	—	—	0.102
Differences .....		0.0035	0.0035	0.0017			

The figures show that a proportionality between the duration of the action and the quantity of substance transformed exists in the early stages of the action, but that this relationship ceases to hold in experiment *A*, when a quantity between 0.0197/0.1175 and 0.0235/0.1175 (that is, between 16.8 and 20 per cent.) of the total action has taken place, and in experiment *B*, between the limits 0.0175/0.102 and 0.0192/0.102 (or 17.1 and 18.8 per cent.). Thus the proportionality between duration of action and the quantity of substance transformed holds until 17.1 to 20 per cent. of the total action has taken place.

#### *The Influence of the Quantity of Acting Enzyme.*

The following experiments were carried out in order to determine if a relation similar to the foregoing could be found to exist between the quantity of acting enzyme and that of the substance transformed.

*Experiment A.*—Known volumes of enzyme solution were added to each of 4 portions of extract of known volume, the relative quantities being so arranged that the quantities of enzyme acting on the unit volume of extract in the four experiments were in the ratio of  $1:1\frac{1}{2}:3:6$ . The total volume was made the same in each case by adding water and the action allowed to proceed at the temperature of the air for 5 hours. At the end of this time, the fermented extracts were rendered ammoniacal, oxidised, and the indigotin estimated.

*Experiment B.*—The ratio between the volumes of acting enzyme solution and of extract were the same as in experiment *A*; the respective quantities and the total volumes were, however, decreased.

The action was allowed to proceed for  $3\frac{3}{4}$  hours at the temperature of the air, after which the samples were oxidised and the indigotin estimated as before.

The total indigotin obtainable from 100 c.c. of extract was estimated in each experiment in the manner previously described.

The following table gives the details and results of the experiments :

Number of sample.	Extract.	Enzyme solution.	Water.	Indigotin obtained from 100 c.c. of extract.	Ratios between quantities of enzyme acting on the same vol. of extract.	Ratios between quantities of indigotin obtained from the same vol. of extract.	Total indigotin obtainable from 100 c.c. of extract.
<i>Experiment A.</i>							
I.	450 c.c.	75 c.c.	0	0·011 gram	} 1 : 1·5 } 1 : 2 } 1 : 2	1 : 1·5	0·098 gram
II.	360 "	90 "	75 c.c.	0·016 "		1 : 1·6	
III.	270 "	135 "	120 "	0·026 "		1 : 1·15	
IV.	180 "	180 "	165 "	0·030 "			
<i>Experiment B.</i>							
I.	360 c.c.	60 c.c.	0	0·008 gram	} 1 : 1·5 } 1 : 2 } 1 : 2	1 : 1·5	0·1125 gram
II.	288 "	72 "	60 c.c.	0·012 "		1 : 1·9	
III.	216 "	108 "	96 "	0·023 "			
IV.	144 "	144 "	132 "	0·037 "			

Thus, in both experiments the amounts of indigotin formed from unit volume of extract are proportional to the amounts of acting enzyme in samples I and II, but not in samples III and IV. So that the proportionality ceases to hold in experiment *A* when between 0·016/0·098 and 0·026/0·098 (that is, between 16·3 and 26·5 per cent.) of the total fermentation has taken place, and in experiment *B* between the limits 0·012/0·1125 and 0·023/0·1125 (that is, between 10·6 and 20·5 per cent.). By combining these two results, it is seen that the stage at which the proportionality ceases is reached when between 16·3 and 20·5 per cent. of the total fermentation is complete. This practically coincides with the point at which the proportionality between the time of action and quantity of indigotin formed was found not to hold.

#### *The Influence of Temperature.*

Difficulty was experienced in carrying out temperature experiments owing to the lack of gas and the consequent impossibility of making

use of a thermostat. The following determinations could therefore be made only with a degree of accuracy which was limited by the fluctuation of temperature in vessels placed on a water-bath heated by a spirit burner.

*Determination of the Optimum Temperature.*

In the preliminary experiments, which were carried out in test-tubes, several tubes were prepared containing 4 c.c. of plant extract, and three or four were placed in each of three beakers of water placed on a water-bath, which was heated as regularly as possible by a spirit burner. The beakers were separated from the bath by blocks of wood of varying thickness, according to the temperature required. Before the tubes were put in, the temperature of the water in the beakers was watched until a maximum was reached, which was kept as constant as possible. When the contents of the tubes had arrived at the same temperature as the surrounding water, 2 c.c. of a dilute enzyme solution (prepared without using hide-powder) was added to each tube, the time at which the enzyme was added and the temperature of the baths throughout the experiments being noted. An attempt was first made to obtain comparative measurements of the advance of fermentation by taking a tube from each bath after equal periods of fermentation, adding the same amount of ammonia to each, oxidising with air under the same conditions, and comparing the depth of the blue colour obtained in each case. It seemed probable that the optimum temperature for the action was higher than  $40^{\circ}$ , but it was found that above that temperature the depth of colour produced in this way was inversely proportional to the temperature after the fermentation had proceeded for a few hours; the effect of keeping tubes of fermented extract at temperatures above  $40^{\circ}$  for a few hours was accordingly tried, and it was found that the solution lost its power of forming indigotin on oxidation with air more or less quickly according to the degree of temperature at which it was kept. Evidently, therefore, the substance resulting from fermentation undergoes a more or less rapid change at an elevated temperature whereby it is no longer capable of giving indigotin on oxidation with air. The proposed method had therefore to be abandoned.

The effect of keeping tubes of dilute unfermented extract at temperatures above  $40^{\circ}$  for several hours was now tried, and it was found that no change in the quantity of indigotin which could be obtained by precipitation by the persulphuric acid method was apparent, however high the temperature. This was tested both by colorimetric comparisons and volumetric estimations of the indigotin precipitated from equal volumes of the same extract, which had been

kept at various temperatures. Accordingly the method devised for determining the point at which a fermentation is complete (p. 878) was used, and it was found that the depths of blue produced on adding the same quantities of hydrochloric acid and ammonium persulphate to the filtrates from the atmosphere oxidations were inversely proportional to the quantity of substance fermented. Care was taken that both the atmospheric oxidation and that of the filtrate with persulphuric acid were carried out under identical conditions in every case, and tubes were compared from each bath at equal intervals of time until one of them showed that the fermentation was complete.

The following table shows the temperatures between which the baths fluctuated in each experiment, the one in which the fermentation proceeded most rapidly being printed in bold figures in each case. The fourth column shows the limits between which the optimum temperature could be placed as a result of each experiment coupled with the results of those which had been made previously.

	Bath I.	Bath II.	Bath III.	Limits between which the optimum temperature lies.
<i>Experiment A</i> .....	32° (incubator)	40—45°	<b>50—55°</b>	45° upwards
<i>Experiment B</i> .....	40—45°	<b>50—55</b>	60—65	45—65°
<i>Experiment C</i> .....	42—49	<b>49—57</b>	60—63	49—63
<i>Experiment D</i> .....	48·5—50	55—56	59—63	49—56

Thus, the optimum temperature lies between 49° and 56°.

Attempts were made to confirm this result by volumetric determinations of indigotin. It was thought improbable that correct results could be arrived at by estimations of the indigotin formed by atmospheric oxidation of the extracts fermented at temperatures above 40°, owing to the decomposition which the fermented extract had been found to undergo at such temperatures.

It seemed probable, however, that the required comparisons might be obtained by acting on the filtrates from the indigotin, derived by atmospheric oxidation of the fermented solutions, with hydrochloric and persulphuric acids under identical conditions. In the following experiments, the indigotin obtained in both ways was estimated.

Flasks containing 200 c.c. of plant extract were supported on wooden blocks on a heated water-bath in the same way as the beakers used in the previous set of experiments. When the temperature of the liquid in the flasks had reached a maximum and was fairly constant, 100 c.c. of an enzyme solution was added to each. The temperatures of the liquids were noted throughout the experiment, and at the end of five hours they were cooled rapidly, 5 c.c. of dilute ammonia added, and oxidised by shaking violently for 10 minutes. The solutions were

then neutralised exactly with hydrochloric acid, boiled, and the precipitate filtered off through asbestos, washed thoroughly with hot water, and the indigotin determined as in the previous experiments. The indigotin was precipitated from the filtrates by the persulphuric acid method, care being taken that it was carried out in exactly the same way in each case. Under these conditions the results are strictly comparable, although they do not correspond with the results obtained by fermenting the solutions and oxidising with air.

The following are the details of the experiments:

*Experiment E.*—The limits of temperature in the two flasks were:

Flask I, 43—46°. Flask II, 49—51°.

The results of the indigotin estimations calculated on 100 c.c. of plant extract were:

	Flask I.	Flask II.
By fermentation and atmospheric oxidation.....	0.0069 gram	0.0084 gram
By the persulphuric acid method with the filtrate.....	0.045 „	0.038 „
Sum of the two estimations .....	0.0519 „	0.0464 „

Thus, the superiority of the higher temperature for fermentation is shown both by the relation between the quantities of indigotin produced by oxidising the fermented solutions and that between the quantities obtained by precipitating from the filtrates by the persulphuric acid method. Hence, the optimum temperature is above 46°.

*Experiment F.*—The limits of temperature in the three flasks were:

Flask I, 49—51°. Flask II, 54—57°. Flask III, 57—59°.

The results of the indigotin estimations calculated as before were

	Flask I.	Flask II.	Flask III.
By fermentation and atmospheric oxidation	0.038 gram	0.035 gram	0.031 gram
By the persulphuric acid method with the filtrate	0.0152 „	0.0160 „	0.0176 „
Sum of the two estimations .....	0.0532 „	0.0510 „	0.0486 „

Here, again, the comparative rates of fermentation under the three different conditions of temperature are shown both by the ratio between the quantities of indigotin formed by fermentation and atmospheric oxidation, and by the inverse ratio between the quantities derived from the filtrates by the persulphuric acid method. The conditions which obtained in flask I were clearly the best for fermentation. The optimum temperature is thus below 57°; it lies, therefore, between 46° and 57°.

The sum of the two indigotin estimations is recorded in each case in

order to illustrate the decrease in the total with rise in temperature. This indicates that more of the substance resulting from fermentation is destroyed the higher the temperature, and confirms the conclusion deduced in the preliminary temperature experiments. It is clear, however, that the decomposition is not sufficiently rapid to affect the relation between the estimations of indigotin obtained directly by oxidation of fermented solutions, provided that sufficient enzyme is added to produce sufficient indigotin for volumetric estimation in a moderately short time.

Accordingly, in the following two experiments, the indigotin was not precipitated from the filtrates from the oxidised solutions. The fermented solutions were oxidised with air in the presence of ammonia as before, but were not neutralised before boiling and filtering off the indigotin; 300 c.c. of extract were taken in each case and 10 c.c. of a strong enzyme solution added. The fermentations were allowed to proceed for  $2\frac{1}{2}$  hours. The following table gives the details and results of the experiments, the quantity of indigotin being calculated on 100 c.c. of extract in each case, and the last column showing the limits between which it is possible to place the optimum temperature as a deduction from each experiment, coupled with the results already obtained in the same manner.

		Limits of temperature fluctuation.	Indigotin obtained from 100 c.c. of extract.	Limits between which the optimum temperature lies.
<i>Experiment G</i>	Flask I.	47—48°	0·0252 gram	46—53°
	Flask II.	52—53	0·0237 „	
<i>Experiment II</i>	Flask I.	47—48	0·0242 „	46—51
	Flask II.	50—51	0·0222 „	

Thus, the optimum temperature is found to lie between 46° and 51°. This temperature could not be determined more closely with the apparatus available. The volumetric determinations confirm the result arrived at in the preliminary experiments, and by coupling the conclusions arrived at by the two methods, the optimum temperature is found to lie between 49° and 51°. That is, it is very near to 50°.

*Determination of the Temperature at which the Enzyme is Destroyed.*

Test-tubes containing 2 c.c. of an enzyme solution were placed in a water-bath heated by a small paraffin lamp. In the first set of experiments, the lamp was so adjusted that the temperature of the water in the bath rose through about 7 degrees in 14 minutes, and a tube was withdrawn at the end of each 7 degree rise from 60° upwards. The contents of the tubes were allowed to cool, and then 4 c.c. of a plant extract added to each. After 8 hours, only the first tube with-

drawn—the temperature of which had not risen above  $67^{\circ}$ —showed the colour change indicating that fermentation had taken place, and gave a precipitate of indigo on agitation with air. The temperature at which the destruction of the enzyme takes place lies therefore between  $60^{\circ}$  and  $74^{\circ}$ .

In the second set of experiments, a tube was withdrawn at the end of each rise of 3 degrees from  $59^{\circ}$  to  $74^{\circ}$  and treated as before, a period of about 7 minutes being taken for each of these increments. In this case, all the tubes except the last withdrawn showed fermentation after 5 hours, that in the fourth ( $68-71^{\circ}$ ) being much inhibited. The point of destruction of the enzyme lies therefore between  $68^{\circ}$  and  $74^{\circ}$ .

Finally, the lamp used in heating the bath was so adjusted that a rise in the temperature of the water through 1 degree took 3 to  $3\frac{1}{2}$  minutes, and tubes were withdrawn at the end of every degree rise from  $68^{\circ}$  to  $73^{\circ}$ . The intervals corresponding with these increments of temperature were :

Tube I.	$68-69^{\circ}$	3 minutes.	Tube IV.	$71-72^{\circ}$	$3\frac{1}{2}$ minutes.
„ II.	$69-70$	3	„ V.	$72-73$	$3\frac{1}{2}$ „
„ III.	$70-71$	$3\frac{1}{2}$ „			

After 6 hours, Tubes I, II, and III showed fermentation, whilst Tubes IV and V showed none; the fermentation was clearly inhibited in No. III. The temperature at which the enzyme is destroyed in neutral solution in  $3\frac{1}{2}$  minutes is thus between  $70^{\circ}$  and  $72^{\circ}$ , or almost exactly  $71^{\circ}$ .

#### *The Influence of Foreign Substances.*

It was found that the influence of a foreign substance on a fermenting extract containing it could be clearly followed by comparing the course of the colour changes taking place in the solution with those in a second specimen of the same extract, fermenting under conditions differing only in the absence of the foreign substance the influence of which was to be determined. In the experiments now to be described, the change from the brown of the unchanged extract to the green of the fermented one took place in a very few minutes under normal conditions. In an experiment where no colour change was apparent in the same time, the fermentation was “inhibited,” and if no change took place in an hour it was considered to be “much inhibited.” If after 3 hours the colour was still unaltered, it was found that no action took place however long the mixture might be allowed to remain. In no case was the addition of a foreign substance found to accelerate the onset or course of the action.

*Influence of Acids, Alkalis, and Neutral Salts.*

The following substances were used in 5 per cent. solutions: hydrochloric acid, acetic acid, sodium carbonate, caustic soda, and sodium acetate.

Test-tubes were prepared containing 2 c.c. of plant extract and 2 c.c. of an enzyme solution, and 1 c.c. of one of the 5 per cent. solutions was added to each; as a check, 1 c.c. of water was added to a sixth tube, all being allowed to remain at the temperature of the air. Only the tube containing sodium acetate showed normal fermentation; the others remained unaltered. The solutions of acids and alkalis were now diluted 10 times and the experiments repeated with the diluted solutions exactly as before, so that now each tube contained 0.1 per cent. of a foreign substance. In this case, hydrochloric acid had a powerful inhibitory effect on the fermentation, and acetic acid a less powerful one, whilst both the alkalis stopped the action entirely. The acid and alkaline solutions were again diluted 10 times and the experiments repeated, each tube now containing 0.01 per cent. of the foreign substance. This resulted in a normal course of action in the case of the two acids, but inhibition in the case of the alkalis.

Finally, 0.1 per cent. solutions of the alkalis were obtained by diluting those used in the last set of experiments 5 times; 1 c.c. of each of these added to tubes prepared as before was found to have no effect on the fermentation.

The results may be summarised as follows:

Percentage quantity of foreign substance added.	Hydrochloric acid.	Acetic acid.	Sodium carbonate.	Caustic soda.	Sodium acetate.
1 per cent.	Destroyed	Destroyed	Destroyed	Destroyed	Normal
0.1 „	Much inhibited	Inhibited	Destroyed	Destroyed	Normal
0.01 „	Normal	Normal	Inhibited	Much inhibited	Normal
0.005 „	Normal	Normal	Normal	Normal	Normal

Thus, the alkalis have a more inhibitory effect on the action than the acids, and the caustic alkali than the carbonate. Hydrochloric acid acts more energetically than acetic acid, and sodium acetate up to 1 per cent. is without effect on the action.

To determine whether these effects of acids and alkalis on the fermentation were due to an action on the enzyme or on the glucoside, or to an actual inhibitory effect on the interaction of these substances, the following experiments were carried out.

Two tubes were prepared containing 2 c.c. of an enzyme solution and 2 c.c. of water. To one, 1 c.c. of 0.5 per cent. hydrochloric acid

was added (tube A), and to the other 1 c.c. of 0.5 per cent. caustic soda (tube B). After ten minutes, the hydrochloric acid was exactly neutralised with 0.5 per cent. caustic soda and the caustic soda with 0.5 hydrochloric acid, and then 2 c.c. of plant extract added to each. Also a tube containing 2 c.c. of plant extract and 2 c.c. of water was rendered acid (tube C), and a similar one made alkaline (tube D), and the acid and alkali neutralised after ten minutes precisely as before, 2 c.c. of enzyme solution being added to each after neutralisation. A check tube was prepared containing 2 c.c. of plant extract and 2 c.c. of enzyme solution, and made up to the same volume as the other four tubes. All were kept at the temperature of the air.

It was found that tube B fermented quite normally. In tube C, the action was much inhibited, but a slight fermentation took place after 3 hours. In tubes A and D the action was entirely stopped.

It was clear, therefore, that 0.1 per cent. of caustic soda was without effect on the enzyme, but that it was destroyed by the same quantity of hydrochloric acid, and that the plant extract was not subject to fermentation after the action of 0.1 per cent. of caustic soda, and only slightly so after the action of 0.1 per cent. of hydrochloric acid. On adding a solution of ammonium persulphate to tubes C and D (after acidifying the latter), a precipitate of indigotin was produced in each case, showing that the power of forming indigotin by chemical means is not destroyed in the plant extract by the action of the acid and alkali added, although the glucoside appears to undergo some change under their influence whereby it is no longer subject to fermentation by the enzyme.

#### *Influence of Antiseptic Substances.*

Tubes containing 2 c.c. of plant extract and 2 c.c. of an enzyme solution were prepared as before, and 1 per cent. of each of the following compounds was added: formaldehyde (commercial solution), chloral hydrate, phenol, chloroform, hydrocyanic acid, and boracic acid.

In each case, the action of the enzyme was inhibited. The comparative inhibitory powers of the substances as judged by the comparative rates at which fermentation was set up in the tubes is indicated by the order in which the names of the substances are placed in the foregoing list, formaldehyde having the greatest influence and boracic acid the least. In the cases of formaldehyde and chloral hydrate, not only did the action set in very slowly, but the compound resulting from the fermentation appeared to undergo change under their influence, the contents of the tubes becoming dark brown soon after the change to green had taken place, and giving no indigo when they were rendered

alkaline and oxidised with air. Under the influence of formaldehyde, the power of forming indigotin by the persulphuric acid method was also destroyed in the extract. This was not the case with any of the other compounds employed in these experiments. Boracic acid was almost without effect on the action.

*Comparison with other Glucoside-splitting Enzymes*

Emulsin and myrosin were selected as being the best known representatives of this class of enzymes, and solutions containing them were prepared as follows.

*Emulsin.*

Bitter almonds were divested of their outer coatings, ground as finely as possible, and extracted for 3 hours with twice their weight of cold water containing a little chloroform. The infusion was then filtered and 3 volumes of 85 per cent. alcohol added to the filtrate. The precipitate so produced was filtered off, washed with a mixture of equal volumes of alcohol and water, and then shaken vigorously with water for an hour. After allowing the bulk of the precipitate to settle, the supernatant liquid was filtered. A clear solution containing emulsin, but no amygdalin, was thus obtained.

A solution containing amygdalin was prepared by throwing finely-ground almonds into boiling water, boiling for a few minutes, and filtering. These operations were repeated, when a clear solution containing amygdalin was obtained. The emulsin was, however, entirely destroyed by the repeated boiling.

A solution containing the indigo enzyme and an extract of the indigo-plant in boiling water was prepared as before. Test-tubes containing the following mixtures were then prepared and allowed to remain at the temperature of the laboratory.

- |           |                              |                                  |
|-----------|------------------------------|----------------------------------|
| Tube I.   | Five c.c. amygdalin solution | + 5 c.c. emulsin solution.       |
| Tube II.  | „ „ „                        | + 5 c.c. indigo enzyme solution. |
| Tube III. | „ „ „                        | + 5 c.c. water.                  |
| Tube IV.  | Five c.c. indigo extract     | + 5 c.c. emulsin solution.       |
| Tube V.   | „ „ „                        | + 5 c.c. indigo enzyme solution. |
| Tube VI.  | „ „ „                        | + 5 c.c. water.                  |

After 6 hours, the odour of benzaldehyde and hydrocyanic acid was very intense in tube I, whilst tube II was practically odourless. The contents of tube IV became slightly green, but, by comparison with tube V, it was evident that very little fermentation had taken place. On adding ammonia and shaking with air, only a slight blue colour was produced in tube IV, whilst a heavy blue precipitate separated

in tube V. The control tubes III and VI were quite unchanged. It was clear, therefore, that emulsin can produce the indigo fermentation, but is much less energetic than the enzyme prepared from the indigo-plant. It is very doubtful whether the indigo enzyme has the power of splitting up amygdalin. The characteristic odour accompanying its decomposition is not evident however long its solution remains mixed with a solution of indigo enzyme. This is contrary to Bréaudat's experience in dealing with a solution containing the enzyme which occurs in *Isatis alpina*. He found that this solution decomposes amygdalin in less than 24 hours.

These experiments were subsequently repeated with emulsin and amygdalin obtained from Kahlbaum and the foregoing results confirmed in each particular.

### *Myrosin.*

A solution containing this enzyme was prepared from the seeds of a species of white mustard commonly grown in India (*Brassica Indica*?) in the same way as described for the preparation of a solution of emulsin from bitter almonds, and a solution containing sinigrin and no myrosin was obtained from black mustard seed in the same way as that described for the preparation of the amygdalin solution.

Tubes containing the following mixtures were then prepared and allowed to remain at the laboratory temperature.

Tube I.	Five c.c. sinigrin solution	+ 5 c.c. myrosin solution.
Tube II.	„ „ „	+ 5 c.c. indigo enzyme solution.
Tube III.	„ „ „	+ 5 c.c. water.
Tube IV.	Five c.c. indigo extract	+ 5 c.c. myrosin solution.
Tube V.	„ „ „	+ 5 c.c. indigo enzyme solution.
Tube VI.	„ „ „	+ 5 c.c. water.

After 6 hours, the odour of mustard oil was very strong in tube I, but in no other tube, whilst only tube V showed any sign of fermentation of the indigo extract. It is clear, therefore, that myrosin cannot produce the indigo fermentation nor can the indigo enzyme ferment sinigrin.

### *Summary.*

It has been shown that, although there are several kinds of bacteria capable of producing the indigo fermentation, some of which are invariably present in an infusion of the plant, the action is in the main dependent on a specific enzyme occurring in the plant-cells. This enzyme acts on a glucoside also occurring in the plant-cells, producing a substance capable of giving indigotin by oxidation with air,

and a reducing sugar. The properties of this enzyme do not appear to be identical with those of any enzymes hitherto described, but it is best left unnamed until the glucoside on which it acts and the products of its action have been more closely identified. The action appears to take a similar course and to be characterised by similar variations with temperature and changes in the medium in which it takes place like that of other enzymes. No evidence of the existence of an oxydase in the indigo-plant was found, but a thorough examination of the plant for a substance of this nature is a matter for future investigation.

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XC.—*Studies in the Camphane Series. Part XIV.*  
*isoNitrosocamphor.*

By MARTIN ONSLOW FORSTER.

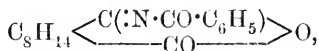
AT the conclusion of a paper dealing with the four dioximes of camphorquinone (Trans., 1903, 83, 514), I described a new form of *isonitrosocamphor*, which was produced on hydrolysing one of the two substances obtained by the action of *m*-nitrobenzoyl chloride on ordinary *isonitrosocamphor*, prepared by the method of Claisen and Manasse (*Annalen*, 1893, 274, 71).

The relationship between the two substances required further investigation, although a preliminary study suggested stereochemical rather than structural isomerism. Moreover, it was not clear whether the new modification arose from the well-known isomeride, or whether, in association with that substance, it constitutes the product of the action of amyl nitrite and sodium upon a solution of camphor in ether.

The results described in the present communication point conclusively to the latter alternative. It is true that fractional crystallisation fails to isolate the new modification from the mixture, but the production of two benzoyl and *m*-nitrobenzoyl derivatives, followed by fractional crystallisation and separate hydrolysis of these, offers a means of obtaining the substance in question; it melts at 114°, and changes at about 135° into the stable *isonitrosocamphor*, which melts at 152°.

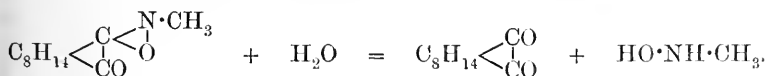
If these two compounds are treated with benzoyl chloride in pyridine, the more fusible, unstable modification yields the yellow benzoyl derivative (m. p. 105–106°), whilst the isomeride furnishes

the colourless benzoyl derivative (m. p. 136°). Unlike the parent substance, the yellow benzoyl compound does not change into the isomeric derivative when heated; hydrolysis with alcoholic ammonia regenerates the unstable *isonitrosocamphor*, mixed with the stable modification, which is produced alone when alcoholic potash is used. The colourless benzoyl derivative, on the other hand, does not give rise to the stable *isonitrosocamphor* on hydrolysis, yielding solely derivatives of *α*-camphornitrilic acid; nevertheless, it is reduced to aminocamphor, yields the *β*-dioxime with hydroxylamine, and is converted into the anhydride of *isonitrosocamphor* when heated in dry benzene with the potassium derivative. Its relation to the *isonitrosocamphor* from which it is derived, therefore, must be a close one, and its representation as benzoyl camphor*iso*imide,



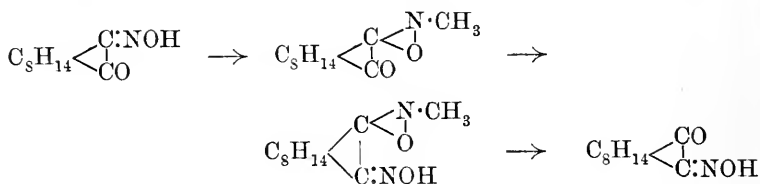
becomes improbable, particularly as the hydrochloride of camphor*iso*imide, when dissolved in pyridine and treated with benzoyl chloride, does not yield the colourless compound obtained from *isonitrosocamphor*. On the other hand, although there can be no doubt that the relation between the two *isonitroso*-derivatives of camphor is that of the two benziloximes, it is difficult to believe that the colourless benzoyl derivative is not structurally different from the yellow one. The colour distinction, and the readiness with which the ring is disrupted on hydrolysis, point to a constitutional difference which still remains obscure.

By acting on either modification of *isonitrosocamphor* with methyl iodide in presence of silver oxide, I have obtained a crystalline methyl derivative which appears to correspond with the colourless benzoyl derivative, since hydrolysis converts it into *α*-camphornitrilic acid without regenerating *isonitrosocamphor*. It also is colourless, and yields aminocamphor on reduction. If the methylation is conducted in presence of alcoholic alkali, the formation of this O-ether becomes subsidiary to that of a *N*-methyl ether, an oil which yields methylaminocamphor on reduction, and is hydrolysed very readily by acids and alkalis, forming camphorquinone and *β*-methylhydroxylamine.



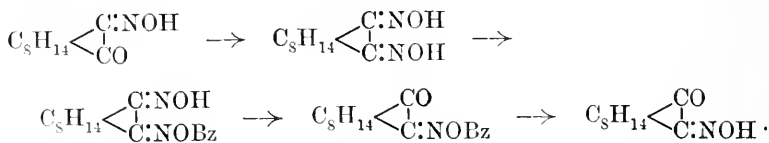
The readiness with which camphorquinone or a derivative is obtained from this ether is remarkable. Both hydroxylamine and phenylhydrazine eliminate the nitrogen, and the attempts to prepare a

structural isomeride of *isonitrosocamphor* on the lines indicated by the formulæ



have therefore failed, ordinary *isonitrosocamphor* and the  $\beta$ -dioxime of camphorquinone being the sole products.

With the same object in view, a number of acyl derivatives of the dioximes have been prepared, in the hope that a monacyl derivative might be found which would yield with nitrous acid an acyl *isonitrosocamphor* distinct from those already known.



The most promising of these was the monobenzoyl derivative of the  $\gamma$ -dioxime, but unfortunately nitrous acid adds nitrogen instead of eliminating it.

It has been found that potassium ferricyanide distinguishes between the two *isonitrosocamphors*, oxidising the unstable modification more quickly than the stable one. By using the ferricyanide in amounts insufficient for complete oxidation, this process becomes a convenient one for isolating the stable *isonitrosocamphor*, which may be precipitated unchanged from the filtered liquid.

## EXPERIMENTAL.

### *The O-Methyl Ether of isoNitrosocamphor.*

Thirty-six grams of commercial *isonitrosocamphor* were dissolved in 90 grams of methyl iodide, mixed in a reflux apparatus with enough dry ether to form a clear solution. Sixty grams of silver oxide were then added in small quantities, the vigorous action which took place being allowed to subside after each addition; finally, the mixture was heated during 2 hours and submitted to a current of steam. When the ether and remaining methyl iodide had passed over, a colourless, crystalline solid slowly distilled, and weighed 35 grams. On recrystallisation from alcohol, it was obtained in large, transparent, rectangular plates, melting at 107°.

0.1726 gave 11.4 c.c. nitrogen at 20° and 742 mm.  $N = 7.37$ .

$C_{11}H_{17}O_2N$  requires  $N = 7.18$  per cent.

A solution containing 0.5025 gram in 25 c.c. of chloroform at 18° gave  $\alpha_D 7^{\circ}57'$  in a 2-dm. tube, whence  $[\alpha]_D + 197.7^{\circ}$ .

The methyl ether obtained in this way dissolves readily in light petroleum, benzene, chloroform, or ethyl acetate, and in hot methyl and ethyl alcohols; it is moderately soluble in boiling water, from which it separates completely on cooling. After boiling with alcohol and concentrated hydrochloric acid during one hour, the liquid does not reduce Fehling's solution, but contains ethyl  $\alpha$ -camphornitrilate. Hydrolysis with alcoholic sodium ethoxide yields no trace of isonitrosocamphor, the only products being  $\alpha$ -camphornitrilic acid and its sodium salt. A solution in glacial acetic acid is indifferent towards nitrous acid, and the solid substance does not yield hydrogen bromide when treated with boiling bromine, even in the presence of iron wire.

Phenylhydrazine has no action on the substance under conditions which favour the production of a phenylhydrazone from isonitrosocamphor.

*Reduction.*—Twenty-five grams were dissolved in 250 c.c. of glacial acetic acid, and kept cool during the addition of 40 grams of zinc dust. After an interval of 12 hours, the excess of acetic acid was removed by steam, and sufficient alkali added to liberate the base, 15 grams of which were obtained. It distilled at 242° under 758 mm. pressure, forming a waxy solid which begins to soften at about 70°, but does not become completely fluid until 110°; the aqueous solution turns red litmus blue, and reduces Fehling's solution on boiling.

In order to complete the identification of this substance with aminocamphor, the benzoyl derivative was prepared by the Schotten-Baumann process, and melted at 132°.

0.3027 gave 14.5 c.c. nitrogen at 18.5° and 756 mm.  $N = 5.49$ .

$C_{17}H_{21}O_2N$  requires  $N = 5.17$  per cent.

The melting point is 8° lower than that given by Claisen and Manasse (*loc. cit.*, 94), but is not depressed by admixture with a specimen of benzoylaminocamphor prepared by the Schotten-Baumann process from aminocamphor obtained by reducing isonitrosocamphor.

*Action of Hydroxylamine.*—Twenty grams were dissolved in 300 c.c. of absolute alcohol, and heated during 10 hours in a reflux apparatus with a mixture of 15 grams of hydroxylamine hydrochloride and 25 grams of anhydrous sodium acetate in the minimum quantity of

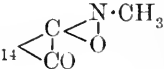
water. On evaporating the alcohol, there remained a sticky, transparent product which was washed with water and treated with a 5 per cent. solution of sodium hydroxide in quantity sufficing to dissolve the oxime, leaving 9 grams of unaltered methyl ether of isonitrosocamphor. The filtrate from the latter was saturated with carbon dioxide, the viscous product gradually hardening on exposure to air; treatment with a very small quantity of cold alcohol gave 4 grams of a colourless, crystalline substance, melting at  $188^{\circ}$ .

0.2198 gave 25.7 c.c. nitrogen at  $19^{\circ}$  and 761 mm.  $N = 13.45$ .

$C_{11}H_{18}O_2N_2$  requires  $N = 13.33$  per cent.

A solution containing 0.6117 gram in 25 c.c. of chloroform at  $20^{\circ}$  gave  $\alpha_D - 4.4'$  in a 2-dcm. tube, whence  $[\alpha]_D - 95.3^{\circ}$ .

The compound is insoluble in hot water, but dissolves very readily in absolute alcohol, from which it separates slowly in well-formed, transparent, six-sided prisms; it crystallises from dilute alcohol in minute, silky needles. The solution in 2 per cent. sodium hydroxide does not give a coloured precipitate with ferrous sulphate.

The N-Methyl Ether of iso-Nitrosocamphor,  $C_8H_{14}$  .

It is well known that isonitrosocamphor, in common with certain other oximino-derivatives of cyclic ketones, does not lose hydroxylamine when heated with hydrochloric acid, the nitrogen remaining combined with carbon in the form of an amido-group. Two processes have been described by which the oximino-group may be eliminated and camphorquinone obtained (Claisen and Manasse, *loc. cit.*, 83), but in neither of these is the nitrogen recovered as hydroxylamine. The following experiment shows how isonitrosocamphor may be resolved into camphorquinone and a derivative of hydroxylamine.

Thirty grams of recrystallised isonitrosocamphor were dissolved in 150 c.c. of absolute alcohol to which 3.9 grams of sodium had been added; the liquid was then heated with 25 grams of methyl iodide. When the dark red colour had changed to pale yellow, the alcohol was removed on the water-bath, and the volatile product distilled in steam. Five grams of the solid methyl derivative were collected in this way, whilst the residual liquid, amounting to 400 c.c., was neutral, clear, and scarcely coloured. On adding dilute sulphuric acid, a faint yellow coloration was developed, intensifying rapidly when the solution was heated on the water-bath; in a few minutes, a bulky, crystalline precipitate of camphorquinone was produced, weighing, with the quantity obtained on distilling the filtrate, 17 grams. The

residual liquid was evaporated, rendered alkaline, and distilled into 20 c.c. of hydrochloric acid diluted with water, which deposited  $\beta$ -methylhydroxylamine hydrochloride on evaporation.

This result could only arise from the hydrolysis of a *N*-methyl ether of isonitrosocamphor, produced by the action of methyl iodide in presence of sodium ethoxide; experiments were therefore made with the object of isolating this compound, and the following process was finally adopted.

Fifty grams of isonitrosocamphor were dissolved in 250 c.c. of absolute alcohol to which 6.5 grams of sodium had been added, the cold solution being treated with 42 grams of methyl iodide, and heated on the water-bath until the deep red colour had changed to pale brown. The alcohol and unused iodide were then distilled off, and a current of steam passed through the residue, which furnished 7.5 grams of the solid methyl derivative in the course of 3 or 4 hours. The residual solution when cooled and filtered measured 700 c.c., and although indifferent to cold Fehling's solution, underwent oxidation on boiling; it became turbid on heating, and also when treated with cold concentrated solutions of sodium hydroxide and of sodium carbonate. Accordingly, 350 grams of washing soda were dissolved in the cold liquid, the precipitated oil extracted twice with ether, the extract dried with calcium chloride, filtered without delay, and evaporated, when 28 grams of a pale golden oil were deposited. It is necessary to remove the ethereal solution as quickly as possible from the calcium chloride, because the *N*-methyl ether combines with that salt. In one experiment involving 50 grams of isonitrosocamphor, the ethereal solution remained 2 days in contact with the calcium chloride, and on filtering and evaporating the ether, only 5 grams of oil were deposited; but on dissolving in water the solid residue which had been thoroughly washed with ether, the missing oil was recovered.

The compound obtained by the foregoing method is a pale golden, limpid oil, which is less dense than water, and is practically odourless. It is not volatile in steam, and decomposes when distilled under atmospheric pressure; some decomposition occurs under 430 mm. pressure, as, although the temperature remains constant at  $233^{\circ}$ , the distilled liquid is bright yellow and has a faint odour of an isonitrile. The specimen for analysis was therefore not distilled, but left in the desiccator during several weeks.

0.1606 gave 0.3990  $\text{CO}_2$  and 0.1284  $\text{H}_2\text{O}$ .  $\text{C} = 67.75$ ;  $\text{H} = 8.88$ .

$\text{C}_{11}\text{H}_{17}\text{O}_2\text{N}$  requires  $\text{C} = 67.70$ ;  $\text{H} = 8.72$  per cent.

A solution containing 1.1376 grams in 25 c.c. of chloroform at  $21^{\circ}$  gave  $\alpha_D^{25} 25^{\circ}28'$  in a 2-dm. tube, whence  $[\alpha]_D^{25} + 279.8^{\circ}$ .

*Reduction.*—Twenty-five grams were dissolved in 250 c.c. of glacial

acetic acid, cooled with melting ice, and treated with 40 grams of zinc dust in small quantities. After 12 hours, the liquid was heated during 1 hour on the water-bath, and distilled in steam until the acetic acid had been removed; excess of sodium hydroxide was then added to the residual liquid and the base rapidly distilled in steam. Caustic alkali was added to the distillate before extracting with ether, and the residue left on evaporating the solvent weighed 18 grams. The base is a colourless oil, which boils at  $237\text{--}238^\circ$  under 760 mm. pressure, considerably lower, therefore, than the specimen of methylaminocamphor obtained by Duden and Pritzkow (*Ber.*, 1899, 32, 1538). The *platinichloride* crystallises from alcohol in silky, red needles, and blackens at  $115^\circ$ .

0.2346 gave 0.0588 Pt.  $\text{Pt} = 25.06$ .

$(\text{C}_{11}\text{H}_{19}\text{ON})_2\text{H}_2\text{PtCl}_6$  requires  $\text{Pt} = 25.22$  per cent.

*Action of Hydroxylamine.*—It has been explained that the readiness with which the *N*-methyl ether undergoes hydrolysis suggested the possibility of obtaining the structural isomeride of *isonitrosocamphor* in which the positions occupied by the oximino-group and ketonic oxygen atom are interchanged; many attempts have been made, therefore, to prepare the oxime of the *N*-methyl ether.

A cold aqueous solution was treated with excess of hydroxylamine hydrochloride and sufficient sodium carbonate to decompose the salt, but even on warming no change occurred.

An alcoholic solution of the ether was then treated with hydroxylamine (1 mol.) in the same solvent, but the only product which could be isolated was an oil; on heating this with alcoholic sodium ethoxide, and precipitating with carbon dioxide, there was obtained a dark red powder, forming with 2 per cent. sodium hydroxide an intense brown solution from which ferrous sulphate precipitated a dark brown substance. This is extremely soluble in organic media, excepting petroleum, and as it is indifferent towards nitrous acid, which should yield camphorquinone if it were a monoxime, its investigation was abandoned.

An attempt to eliminate  $\beta$ -methylhydroxylamine from the oil by means of benzaldehyde having failed, the action of alcoholic hydrochloric acid was studied. Eleven grams were dissolved in 45 c.c. of absolute alcohol and treated with 5 c.c. of concentrated hydrochloric acid. After 36 hours, the solution was evaporated, water added to the residue, which was then shaken with ether, the ethereal solution being next extracted with 2 per cent. sodium hydroxide; from this solution, carbon dioxide precipitated 2 grams of ordinary *isonitrosocamphor*, whilst the ether deposited only the *N*-methyl derivative of that substance. Finally, 4 grams of the *N*-methyl ether dissolved in

alcohol were heated on the water-bath with 2 grams of hydroxylamine hydrochloride which had been mixed with 2.5 grams of sodium acetate. After 2 hours, the liquid was evaporated and the residue was found to consist of isonitrosocamphor and the  $\beta$ -dioxime of camphorquinone, with some unaltered methyl derivative.

From these experiments, it appears to be impossible to induce the *N*-methyl ether to combine with hydroxylamine without displacing the methylhydroxylamine residue.

*Oxidation of isoNitrosocamphor with Potassium Ferricyanide.*

The brief notice of the change by which nitrocamphor may be obtained from isonitrosocamphor (Trans., 1903, 83, 532) mentioned the occurrence of a precipitate when potassium ferricyanide is added to a solution of the isonitroso-compound in caustic alkali. With the quantities there specified, this precipitate disappears within 15 minutes, and several unsuccessful attempts to isolate the substance were made before the proper conditions could be ascertained. Ultimately it was found that it is the excess of alkali which causes the precipitate to disappear, and that if only one molecular proportion is employed, the intermediate compound remains undissolved. Moreover, by using potassium ferricyanide in a quantity smaller than the theoretical amount, no diminution occurs in the yield of oxidation product, and a considerable proportion of isonitrosocamphor may be recovered from the filtrate.

The following conditions were finally adopted. Twenty-five grams of recrystallised isonitrosocamphor were dissolved in 100 c.c. of water containing 6.5 grams of sodium hydroxide; 35 grams of potassium ferricyanide dissolved in 100 c.c. of water were then added, producing immediately a precipitate so bulky that there was not time for the liquids to mix completely. Within a minute, however, the solid had become more compact and was then rapidly filtered, water being added at short intervals and before the liquid had passed through; this treatment is necessary, because the solid substance becomes hot spontaneously if allowed to remain in contact with the mother liquor during many minutes. When the filtrate was only pale yellow, the precipitate was transferred to another funnel, filtered at the pump, and finally drained on porous earthenware. This process yields 5 grams of the air-dried oxidation product, and 15 grams of isonitrosocamphor are recovered from the filtrate on acidification.

As obtained in the manner described, the substance is a pale yellow, impalpable powder, dissolving very readily in organic media excepting petroleum. It is insoluble in water and in dilute sulphuric acid; a very small proportion is dissolved by a 10 per cent. solution of sodium

hydroxide after 24 hours' suspension, whilst a 40 per cent. solution produces a clear liquid in 2 hours. The dissolution in alkali is not hastened by the presence of either *isonitrosocamphor* or potassium ferricyanide. The chloroform solution is indifferent towards bromine, and the alcoholic solution liberates iodine from potassium iodide; the dry substance gives Liebermann's reaction for nitroso-compounds. When treated with an alcoholic solution of sodium hydroxide, it develops an intense violet coloration which quickly changes to brown; this behaviour is not shown towards alcoholic ammonia.

Great difficulty has been experienced in recrystallising the substance, as it decomposes rapidly when dissolved. By warming 2 grams with 6 c.c. of ethyl acetate, filtering at the pump, and rapidly cooling the filtrate, about 1 gram of minute, pale yellow needles may be obtained; these must be filtered immediately and drained on earthenware, the yield being diminished if a delay of a few minutes occurs during the double filtration, which should not occupy more than 20 minutes, as the recrystallised substance, when left in contact with the mother liquor, rapidly disappears. The solution in ethyl acetate is deep red when warm, and becomes pale yellow on cooling; the crystals melt at  $96^{\circ}$ , forming a deep red liquid which immediately evolves gas and becomes pale yellow.

0.1695 gave 0.4128  $\text{CO}_2$  and 0.1216  $\text{H}_2\text{O}$ .  $\text{C} = 66.42$ ;  $\text{H} = 7.97$ .

0.1781 „ 11.3 c.c. nitrogen at  $17^{\circ}$  and 755 mm.  $\text{N} = 7.31$ .

$\text{C}_{20}\text{H}_{28}\text{O}_4\text{N}_2$  requires  $\text{C} = 66.66$ ;  $\text{H} = 7.77$ ;  $\text{N} = 7.77$  per cent.

Although analysis indicates that the crystals have the composition of *isonitrosocamphor* peroxide, there is reason to believe that the original product of oxidation becomes modified during filtration and recrystallisation; it is probable that the initial substance is a hydrate, because a specimen dried on porous earthenware becomes moist on exposure to air and loses weight in the desiccator, the loss of water being accompanied by the production of a colourless compound (m. p.  $172-173^{\circ}$ ). This product was found by examining a specimen of the uncrystallised oxidation compound which had remained exposed to air during 3 weeks. Twenty-five grams were extracted with a 5 per cent. solution of sodium hydroxide, which left a yellow residue; this was dissolved in dilute alcohol, from which it separated in needles, and, on recrystallisation, a colourless substance was obtained melting and evolving gas at  $172-173^{\circ}$ .

0.1904 gave 0.4495  $\text{CO}_2$  and 0.1320  $\text{H}_2\text{O}$ .  $\text{C} = 64.38$ ;  $\text{H} = 7.76$ .

0.1692 „ 11.2 c.c. nitrogen at  $20^{\circ}$  and 740 mm.  $\text{N} = 7.37$ .

$\text{C}_{20}\text{H}_{28}\text{O}_5\text{N}_2$  requires  $\text{C} = 63.83$ ;  $\text{H} = 7.45$ ;  $\text{N} = 7.45$  per cent.

This compound gives all the phases of an intense Liebermann re-

action. The substance was also produced on treating the freshly precipitated oxidation product with cold dilute nitric acid (sp. gr. 1·07), which converts the yellow powder into a dull green paste; this becomes subsequently hard and pale yellow, and, when recrystallised from dilute alcohol, melts at 172—173° evolving gas.

The dilute solution of sodium hydroxide from which the foregoing substance was filtered, was saturated with carbon dioxide, which precipitated 1 gram of minute crystals, separating from boiling alcohol in minute, well-formed prisms which decompose at 262°, forming a turbid paste.

0·1578 gave 0·3576 CO<sub>2</sub> and 0·1148 H<sub>2</sub>O. C = 61·80; H = 8·08.

0·2098 „ 25·8 c.c. nitrogen at 17·5° and 764 mm. N = 14·31.

C<sub>20</sub>H<sub>30</sub>O<sub>4</sub>N<sub>4</sub> requires C = 61·54; H = 7·70; N = 14·36 per cent.

The production of this compound is noteworthy, as it involves intramolecular addition of nitrogen to the oxidised isonitrosocamphor. At first, it was believed to be the  $\beta$ -dioxime of camphorquinone, but the solution in 2 per cent. sodium hydroxide gives no distinctive precipitate with ferrous sulphate. It is insoluble in hot petroleum, sparingly soluble in boiling water, and moderately soluble in boiling alcohol.

*Action of Phosphorus Oxychloride.*—When the air-dried oxidation product is treated with phosphorus pentachloride, an extremely vigorous action takes place; torrents of gas are evolved, and a brown oil results, becoming semi-solid only after prolonged treatment with water. With phosphorus oxychloride, however, the action is more moderate, and a crystalline compound has been obtained.

Seventeen grams of a specimen of the oxidation product, which had been prepared 24 hours previously and was quite powdery, were added in small quantities to 40 grams of phosphorus oxychloride immersed in melting ice; the substance dissolved immediately without effervescence, and, on pouring the pale brown liquid on to crushed ice, the precipitated solid soon became granular. The filtered substance was treated with 60 c.c. of 5 per cent. sodium hydroxide, and then weighed 6 grams; after two recrystallisations from absolute alcohol with an intermediate one from dilute alcohol, it was obtained in pale brown, spherical aggregates melting and evolving gas at 207°.

0·1858 gave 0·4482 CO<sub>2</sub> and 0·1313 H<sub>2</sub>O. C = 65·75; H = 7·91. ,

0·1696 „ 12·0 c.c. nitrogen at 17° and 747 mm. N = 8·06.

C<sub>20</sub>H<sub>28</sub>O<sub>4</sub>N<sub>2</sub> requires C = 66·66; H = 7·77; N = 7·77 per cent.

The substance is very readily soluble in acetone, benzene, chloroform, and hot alcohol, the solutions having no effect on potassium iodide; the Liebermann reaction is very intense in all three stages.

*Action of Hydroxylamine.*—Ten grams of the freshly precipitated

oxidation product were dissolved in warm alcohol and treated with 5 grams of hydroxylamine hydrochloride in 50 per cent. alcohol. The liquid remained clear, but the deep orange colour changed immediately to pale yellow, and slight effervescence occurred. After 1 hour, the solution was filtered and diluted until turbid, when minute, colourless needles separated in the course of several days. This product was dissolved in sodium hydroxide, reprecipitated by acids, and found to consist of a mixture of the  $\alpha$ - and  $\beta$ -dioximes of camphorquinone; *iso*-nitrosocamphor was not present.

*Reduction.*—When the freshly prepared substance is suspended in 20 per cent. sodium hydroxide and treated with zinc dust, aminocamphor is quickly produced. In another experiment, the compound was suspended in glacial acetic acid, and immediately poured on a mixture of crushed ice and zinc dust. After 12 hours, the substance had dissolved almost completely, and the filtered liquid contained aminocamphor and *iso*-nitrosocamphor.

*The Stable isoNitrosocamphor, m. p. 152°.*

In studying the product of oxidising *isonitrosocamphor* with potassium ferricyanide under the conditions just described, a considerable amount of recovered material was accumulated. On dissolving this in sodium hydroxide, it was noticed that the colour of the solution was much paler than that of the original *isonitroso*-derivative; moreover, on adding the ferricyanide, there was a perceptible delay in the formation of a precipitate, although the yield of insoluble material is not diminished. On recovering the *isonitrosocamphor* which remained unaltered by this second treatment with ferricyanide, it was found to display the same peculiarities more clearly; the solution in alkali was canary-yellow instead of deep orange-red, and, on treating it with ferricyanide under the prescribed conditions, precipitation was not complete until 4 or 5 minutes had elapsed. With dilute sulphuric acid, the filtrate yielded a colourless oil, which quickly hardened; this was crystallised from benzene, and recrystallised from light petroleum (b. p. 50–90°), which deposited snow-white needles melting at 152°, and giving  $[\alpha]_D + 197.0^\circ$ , identical with *isonitrosocamphor* obtained by heating the mixture of isomerides at 150° and recrystallising the product from petroleum (Forster, *loc. cit.*, 535). By means of selective oxidation with potassium ferricyanide, therefore, it is possible to remove the unstable modification of *isonitrosocamphor* from a mixture of the isomerides, and the following experiments, undertaken with the residual modification (m. p. 152°), show how far the behaviour of the mixture is due to the presence of that substance.

*Benzoylation.*—Five grams dissolved in 25 c.c. of water containing

2.5 grams of sodium hydroxide, when shaken with 5 grams of benzoyl chloride, yielded a snow-white solid almost immediately, instead of a yellow, sticky product which hardened gradually. Recrystallisation from boiling alcohol furnished lustrous leaflets melting at  $136^{\circ}$ , the mother liquor being colourless. The same product was obtained by dissolving 5 grams in 10 c.c. of pyridine, cooling the solution in melting ice, and adding the calculated amount of benzoyl chloride.

*Action of Hydroxylamine.*—Ten grams were dissolved in water containing 9 grams of sodium hydroxide and treated with 10 grams of hydroxylamine hydrochloride, with enough water to bring the volume to 100 c.c. The liquid was left for 4 weeks and was still bright yellow, yielding 6 grams of crystalline precipitate on passing in carbon dioxide, whilst the filtrate gave only a slight sticky precipitate with mineral acid. The colour produced on adding ferrous sulphate to a solution of the carbon dioxide precipitate in 2 per cent. sodium hydroxide suggested the presence of isonitrosocamphor and a dioxime of camphorquinone; the mixture, accordingly, was extracted with 250 c.c. of boiling water, when the residue, weighing 1.5 grams, gave the dioxime coloration with alkali and ferrous sulphate, whilst the filtrate, which gave that characteristic of isonitrosocamphor, deposited colourless needles melting at  $152^{\circ}$ . The portion undissolved by boiling water was extracted with 150 c.c. of hot alcohol, from which the  $\beta$ -dioxime alone separated. From this experiment, it follows that the stable modification of isonitrosocamphor remains for the most part indifferent to hydroxylamine under conditions which transform the unstable isomeride into the  $\gamma$ -dioxime.

*Methylation.*—Eighteen grams were treated with 45 grams of methyl iodide and 35 grams of dry silver oxide in the manner already described, 18 grams of the solid methyl ether being obtained; it melted at  $107^{\circ}$  and gave  $[\alpha]_D + 197.7^{\circ}$  in chloroform.

*Ethylation.*—Ten grams were dissolved in 50 c.c. of absolute alcohol to which 1.3 grams of sodium had been added, and heated with 10 grams of ethyl iodide in a reflux apparatus during half an hour. The colour having disappeared, steam was passed through the liquid, which yielded 5 grams of a colourless solid. On recrystallisation from alcohol, long, lustrous, flat prisms were obtained melting at  $71^{\circ}$ .

A solution containing 0.5026 gram in 25 c.c. of chloroform at  $18^{\circ}$  gave  $a_D 7^{\circ}55'$  in a 2-dm. tube, whence  $[\alpha]_D + 196.9^{\circ}$ .

*Oxidation with Potassium Ferricyanide.*—Although oxidation with potassium ferricyanide in presence of excess of alkali leads to the production of nitrocamphor, this substance is not present in the solution directly the peroxide dissolves, for if the liquid is acidified at this stage, which usually occurs within 15 minutes of mixing the materials,

isonitrosocamphor is regenerated. Two parallel experiments were then made in which 5 grams of isonitrosocamphor (m. p. 152°) were dissolved in 20 c.c. of water containing 1.3 grams of sodium hydroxide, and treated, in one case with 7 grams of ferricyanide in 20 c.c. of water, whilst in the other case 12.5 grams in 40 c.c. were added. Both set to a paste after a few seconds, becoming considerably thinner during the first half-hour, although a moderate proportion remained undissolved after 2 days. In each case, the acidified filtrate gave  $\alpha$ -camphornitrilic acid, and not nitrocamphor, although the last-named substance, when left with potassium ferricyanide and alkali during 2 days, undergoes no change.

*The Unstable isoNitrosocamphor (m. p. 114°).*

Since the discovery of an unstable modification of isonitrosocamphor (Trans., 1903, 83; 534), I have made several attempts to prepare it by other methods, and to improve the yield of substance obtained by the process already described. Although it is much more readily soluble than the stable isomeride in boiling light petroleum, 100 c.c. of which dissolves 1.8 grams of the former and only 0.17 gram of the latter, nevertheless, exhausting with this solvent the mixture of isomerides obtained from camphor, sodium, and amyl nitrite does not remove the more soluble component; as the benzylation experiment indicates the presence of at least 50 per cent. of the latter, it seems probable that the two substances are loosely united with one another, and not merely mixed. Although the unstable modification is produced by hydrolysing the yellow benzoyl derivative with alcoholic ammonia, this process is not to be recommended, and the least unsatisfactory method, which still leaves much to be desired, is the following.

Two grams of yellow *m*-nitrobenzoylisonitrosocamphor are dissolved in 25 c.c. of boiling absolute alcohol, cooled rapidly, and treated with 4 grams of potassium hydroxide in the minimum quantity of water; the crystals which separate on cooling the solution dissolve immediately when the alkali is added, forming an intense red solution. This is evaporated to dryness on the water-bath without delay, the dish being withdrawn directly the alcohol has been removed. The dark brown product obtained from 20 grams of the *m*-nitrobenzoyl derivative which has been treated in this way is dissolved in 100 c.c. of water, and submitted at once to the action of a rapid current of carbon dioxide, which gradually precipitates brown needles; these are filtered at the pump, drained on earthenware without being washed, dried in the desiccator, and extracted several times with 100 c.c. of boiling light petroleum, which deposits 6.5 grams of the isomeride melting at 114°.

It is only by following closely the above prescription that transformation into the modification which melts at  $152^{\circ}$  can be avoided. Experiments in which the evaporating basin was not removed as soon as the alcohol had disappeared, or in which the residue was left 12 hours before dissolving in water, or in which this solution was not treated immediately with carbon dioxide, failed to yield any of the unstable modification, ordinary *isonitrosocamphor* being obtained alone; hydrolysing a cold solution, from which the alcohol was distilled subsequently under reduced pressure, also failed to yield the unstable modification.

A solution of the substance in alkali is coloured much more intensely than that of the stable modification, but the colour gradually fades until the liquid is only pale yellow; this change can be followed in the polarimeter, and is found to proceed less rapidly if the solution is protected from light. For example, 0.2043 gram dissolved in 25 c.c. of 2 per cent. sodium hydroxide at  $20^{\circ}$  gave  $\alpha_D$   $4^{\circ}30'$  in a 2-dcm. tube, whence  $[\alpha]_D + 275.3^{\circ}$ ; after 2 days, this had risen to  $[\alpha]_D + 281.5^{\circ}$ , remaining constant at  $[\alpha]_D + 287.5^{\circ}$ , which was reached after 7 days when the solution was exposed to daylight, requiring many weeks in the dark. A solution containing 0.2653 gram of the stable modification dissolved in 25 c.c. of 2 per cent. sodium hydroxide at  $20^{\circ}$  gave  $\alpha_D$   $6^{\circ}6'$  in a 2-dcm. tube, whence  $[\alpha]_D + 287.3^{\circ}$ , which underwent no change during several weeks.

*Benzoylation.*—The Schotten-Baumann process of benzoylation converts the unstable *isonitrosocamphor* into approximately equal amounts of the colourless derivative melting at  $136^{\circ}$  and the yellow compound melting at  $105^{\circ}$ ; in pyridine, however, the latter substance alone is produced. Two grams were dissolved in 5 c.c. of ice-cold pyridine and treated with 1.6 grams of benzoyl chloride; after an interval of half an hour, the liquid was poured on crushed ice, and the deep yellow semi-solid product drained on earthenware. The substance weighed 2.2 grams, and dissolved completely in boiling light petroleum, which deposited the yellow crystals melting at  $105^{\circ}$ , without a trace of the colourless modification.

*Methylation.*—Two grams of the unstable *isonitrosocamphor* were dissolved in 5 grams of methyl iodide with 5 grams of ether, and treated with 4 grams of silver oxide. There was no perceptible action until the liquid was heated, when silver iodide was quickly produced. On evaporating the ether, *isonitrosocamphor O*-methyl ether was obtained, melting at  $107^{\circ}$ , and identical with the compound from the stable modification.

*Attempt to prepare a Stereoisomeric Camphoroxime.*—Before the isolation of an unstable *isonitrosocamphor* by means of *m*-nitrobenzoyl

chloride was traced to the mixed character of the material employed, it seemed worth while to test the possibility of obtaining a stereoisomeric oxime of camphor by converting ordinary camphoroxime into the *m*-nitrobenzoyl derivative, and hydrolysing this compound under the conditions prescribed above.

Twenty grams of camphoroxime were suspended in 200 c.c. of 10 per cent. aqueous sodium hydroxide and agitated with 28 grams of *m*-nitrobenzoyl chloride, the solid product being crystallised from petroleum and recrystallised from alcohol. The *m*-nitrobenzoyl derivative of camphoroxime was thus obtained in needles melting at 89–90°.

A solution containing 0.4800 gram in 25 c.c. of chloroform at 21° gave  $\alpha_D - 1^\circ 18'$ , whence  $[\alpha]_D - 33.8^\circ$ .

Hydrolysis with alcoholic potash regenerated ordinary camphoroxime, m. p. 118°.

*The Colourless Benzoyl Derivative of iso-Nitrosocamphor.*

Hitherto the benzoyl derivative which melts at 136° has been obtained always in association with the yellow isomeride melting at 105°. Its occurrence as the sole product of benzoylation in pyridine and by the Schotten-Baumann method, when the stable isonitrosocamphor is used instead of Claisen's mixture, makes it difficult to understand how it can be other than a genuine benzoyl derivative of the less fusible modification. Moreover, its behaviour towards hydroxylamine and on reduction excludes the likelihood of its being the benzoyl derivative of camphorisoimide, a possibility which presented itself in view of the transformation by alkalis into  $\alpha$ -camphornitrilic acid.

*Action of Hydroxylamine.*—Five grams were dissolved in alcohol and heated with 10 grams of hydroxylamine hydrochloride and 17 grams of anhydrous sodium acetate in a reflux apparatus during 1 hour, when the solution became pink. Having filtered the sodium chloride, the alcohol was evaporated and water added, the insoluble portion being identified as the  $\beta$ -dioxime of camphorquinone; the filtrate from this product yields benzoic acid on acidification.

*Reduction.*—Twenty-five grams of the colourless benzoyl derivative dissolved in 250 c.c. of glacial acetic acid were treated with 40 grams of zinc dust in small quantities. After 12 hours, the acid was removed by a current of steam, which was again passed through the liquid after adding alkali, the distillate being treated with potassium hydroxide and extracted with ether, which deposited 5 grams of aminocamphor boiling at 242° under 743 mm. pressure; the benzoyl derivative obtained from this base was identified with a specimen prepared from freshly distilled aminocamphor.

*Action of Alcoholic Ammonia.*—When the colourless benzoyl derivative of isonitrosocamphor is covered with alcoholic ammonia, the paste remains colourless, but quickly becomes warm and much thinner without forming a clear solution; colourless crystals then separate, and the ammonia is completely absorbed. The products are ammonium benzoate, ethyl benzoate, ethyl  $\alpha$ -camphornitrilate, and a solid substance remaining undissolved when the filtered crystals are treated with water. It dissolves very readily in hot ethyl acetate, crystallising in long, lustrous needles which melt at  $154^{\circ}$ .

0.2100 gave 0.5362  $\text{CO}_2$  and 0.1558  $\text{H}_2\text{O}$ .  $\text{C} = 69.65$ ;  $\text{H} = 8.30$ .

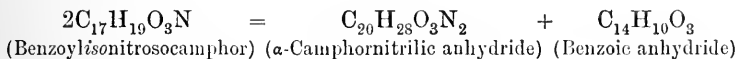
0.2934 „ 21.5 c.c. nitrogen at  $18^{\circ}$  and 741 mm.  $\text{N} = 8.24$ .

$\text{C}_{20}\text{H}_{28}\text{O}_3\text{N}_2$  requires  $\text{C} = 69.77$ ;  $\text{H} = 8.14$ ;  $\text{N} = 8.14$  per cent.

It will be noticed that this substance is isomeric with the anhydrides of  $\alpha$ -camphornitrilic acid and isonitrosocamphor.

*Conversion into the Anhydride of isoNitrosocamphor.*—Ten grams of the colourless benzoyl compound (m. p.  $136^{\circ}$ ) were dissolved in 100 c.c. of dry benzene, and treated with twenty grams of the finely powdered potassium derivative of isonitrosocamphor, when a vigorous action at once ensued; the benzene boiled, and potassium benzoate separated in a gelatinous form. After one hour on the water-bath in a reflux apparatus, the benzene was filtered and evaporated, yielding a yellow syrup from which the anhydride of isonitrosocamphor was obtained by treatment with alcohol. The product was identical with that prepared from the yellow benzoyl compound and the potassium derivative of isonitrosocamphor (Trans., 1903, 83, 530).

*Decomposition by Light.*—It was stated that the specific rotatory power of the colourless benzoyl derivative dissolved in chloroform falls from  $[\alpha]_D + 127.4^{\circ}$  to  $[\alpha]_D + 32^{\circ}$ , when the solution is exposed to light during 56 days (Forster, *loc. cit.*, 527). This change has been further investigated, and found to depend on the production of the anhydride of  $\alpha$ -camphornitrilic acid, obtained by the transformation of isonitrosocamphor anhydride (*loc. cit.*, 531) by heat:



Sixteen grams of the colourless benzoyl derivative were dissolved in about 100 c.c. of dry chloroform, the solution giving  $\alpha_D + 35^{\circ}27'$ . Exposure to sunlight developed a yellow coloration within an hour, and in the course of several days this became very intense, but began to fade after six weeks, the liquid becoming colourless about 3 weeks later; the solution was very acid, and gave  $\alpha_D + 14^{\circ}45'$ . The sticky, yellow residue obtained on evaporating the chloroform was warmed with sodium carbonate and shaken with ether, in which a

colourless solid became suspended; after crystallisation from alcohol, this melted at  $176^{\circ}$ , and was identical with the anhydride of  $\alpha$ -camphornitrilic acid. The sodium carbonate solution gave a mixture of benzoic and  $\alpha$ -camphornitrilic acids.

*Determination of the Molecular Weight.*—This was carried out in benzene, with the following result:

Grams of benzene.	Grams of substance.	Grams of substance in 100 grams of benzene.	Depression of the freezing point.	Molecular weight deduced.
17.54	0.0999	0.57	0.097	288
„	0.3600	2.05	0.345	291
„	0.4401	2.51	0.416	295

The molecular weight is therefore normal, the formula  $C_{17}H_{19}O_3N$  requiring 285.

*The Yellow Benzoyl Derivative of isoNitrosocamphor.*

The exclusive production of the yellow benzoyl derivative (m. p.  $105-106^{\circ}$ ) by the action of benzoyl chloride in pyridine on the unstable *isonitrosocamphor* (m. p.  $114^{\circ}$ ), and the regeneration of the last-named by the action of alcoholic ammonia, establish the relationship between the two substances. In preparing it from the mixture of isomerides obtained by the action of sodium and amyl nitrite on camphor, it is associated with its own weight of the colourless benzoyl derivative (m. p.  $136^{\circ}$ ), which is the exclusive product of the action of benzoyl chloride in pyridine on the stable *isonitrosocamphor* (m. p.  $152^{\circ}$ ); separation of the two benzoyl derivatives is effected by fractional crystallisation from petroleum.

*Decomposition by Light.*—A specimen of the purified benzoyl derivative (m. p.  $105-106^{\circ}$ ) which had been exposed to air during 12 months acquired the odour of benzoic acid, crystals of which could be recognised on the surface of the substance; the product now liberated carbon dioxide from aqueous sodium carbonate. A solution of 10.0083 grams in 250 c.c. of chloroform was accordingly prepared, and exposed to daylight during 9 weeks, the initial rotation  $[\alpha]_D +145.7^{\circ}$  falling steadily until it became constant at  $[\alpha]_D +42.6^{\circ}$ .

This change in specific rotatory power was accompanied by disappearance of colour and development of acidity. A more concentrated solution, containing 25 grams in 250 c.c. of chloroform, exposed side by side with the foregoing specimen, was still bright yellow after nine weeks' exposure, and gave  $[\alpha]_D +81^{\circ}$ , but on diluting it to 2 per cent., it became colourless in a few days, and gave  $[\alpha]_D +42.5^{\circ}$ .

On evaporating the colourless solution, and treating the viscous residue with sodium carbonate to dissolve benzoic acid, an oil was

obtained which distils in steam and appears to be identical with ethyl  $\alpha$ -camphornitrilate. No doubt the yellow benzoyl derivative becomes resolved into benzoic and  $\alpha$ -camphornitrilic anhydrides, the latter being converted into the ethyl ester by the small quantity of alcohol present in the chloroform.

*Molecular Weight.*—A determination of the molecular weight in benzene gave the following result :

Grams of benzene.	Grams of substance.	Grams of substance in 100 grams of benzene.	Depression of the freezing point.	Molecular weight deduced.
17.23	0.1064	0.62	0.122	248
„	0.1953	1.13	0.204	272
„	0.4633	2.69	0.490	269

The formula  $C_{17}H_{19}O_3N$  requires 285.

*Action of Phenylhydrazine on isoNitrosocamphor.*

Claisen and Manasse state that the phenylhydrazone is readily obtained from *isonitrosocamphor* and the base dissolved in 50 per cent. acetic acid (*loc. cit.*, 78). I have been able to confirm this only in connection with the mixture of isomerides, from 90 grams of which there were obtained 40 grams of the phenylhydrazone in 48 hours ; the substance melts at  $138^\circ$  (Claisen and Manasse mention  $130^\circ$ ). No crystalline product was obtainable from the stable isomeride, even after many weeks, and I therefore believe the phenylhydrazone in question to be derived from the unstable *isonitrosocamphor*. Nevertheless, on treating it with benzaldehyde (1 mol.) on the water-bath, and extracting the ethereal solution with dilute sodium hydroxide, carbon dioxide precipitated from this solution the stable *isonitrosocamphor* (m. p.  $152^\circ$ ).

*Acyl Derivatives of the  $\alpha$ -Dioxime.*

*Monacetyl Derivative.*—Ten grams of  $\alpha$ -dioxime were finely powdered and covered with 50 c.c. of cold acetic anhydride, which quickly became warm, and dissolved the substance within 15 minutes. The solution was then poured into 500 c.c. of cold water, the colourless crystals which separated being filtered after an interval of 24 hours. Recrystallisation from a small quantity of hot absolute alcohol gave hard, transparent prisms, which melt and evolve gas at  $148$ — $149^\circ$ .

0.2593 gave 27.0 c.c. nitrogen at  $16^\circ$  and 750 mm.  $N = 12.00$ .

$C_{12}H_{18}O_3N_2$  requires  $N = 11.76$  per cent.

It dissolves very readily in cold absolute alcohol, and very sparingly

in hot petroleum and boiling water, crystallising from the latter in minute prisms.

*Dibenzoyl Derivative.*—The product of benzoylation by the Schotten-Baumann process remained sticky during several days; when quite hardened, it was crystallised from absolute alcohol, which deposited lustrous, white needles melting at  $153^{\circ}$ .

0.2178 gave 13.6 c.c. nitrogen at  $20^{\circ}$  and 773 mm.  $N = 7.27$ .

$C_{24}H_{24}O_4N_2$  requires  $N = 6.93$  per cent.

A solution containing 0.5025 gram in 25 c.c. of chloroform at  $20^{\circ}$  gave  $\alpha_D - 2^{\circ}23'$  in a 2-dcm. tube, whence  $[\alpha]_D - 59.3^{\circ}$ .

It is readily soluble in boiling ethyl acetate and hot glacial acetic acid, crystallising in minute, silky needles from each; boiling petroleum dissolves it sparingly.

#### *Acyl Derivatives of the $\beta$ -Dioxime.*

*Diacetyl Derivative.*—Ten grams of the  $\beta$ -dioxime were suspended in 50 c.c. of acetic anhydride, which dissolved the substance very slowly; after half an hour the temperature rose, and another hour having elapsed the liquid was poured into 200 c.c. of water. When the anhydride had become decomposed, the clear solution was neutralised with solid sodium carbonate, and the solid product crystallised twice from alcohol, forming minute, lustrous needles which melt at  $119^{\circ}$ .

0.2140 gave 0.4662  $CO_2$  and 0.1354  $H_2O$ .  $C = 59.41$ ;  $H = 7.08$ .

$C_{14}H_{20}O_4N_2$  requires  $C = 60.00$ :  $H = 7.14$  per cent.

The substance is optically inactive.

*Dibenzoyl Derivative.*—A solution of the  $\beta$ -dioxime in aqueous potassium hydroxide, when shaken with benzoyl chloride ( $2\frac{1}{2}$  mols.), yields a sticky product which solidifies very slowly. After some days, it hardens, and may be then crystallised from a small quantity of alcohol. As purification proceeds, the solubility decreases to an unusual extent, so that in the final recrystallisation 150 c.c. of boiling alcohol are required to dissolve 5 grams of the substance, of which 4 grams are deposited as the liquid cools.

0.3561 gave 22.1 c.c. nitrogen at  $20^{\circ}$  and 762 mm.  $N = 7.12$ .

$C_{24}H_{24}O_4N_2$  requires  $N = 6.93$  per cent.

The substance is dimorphous, separating from hot, concentrated solutions in slender needles melting at  $189^{\circ}$ , whilst cold, dilute solutions deposit transparent, hexagonal prisms melting at  $191^{\circ}$ ; each form may be converted into the other by recrystallisation from alcohol in the manner indicated.

A solution containing 0.5013 gram in 25 c.c. of chloroform at 20° gave  $\alpha_D$  8' in a 2-dcm. tube, whence  $[\alpha]_D + 3.3^\circ$ .

A different result was obtained on benzoylating in pyridine, the experiment presenting features which I am unable to explain. Seven grams of benzoyl chloride were added to 4.9 grams of the dioxime dissolved in 50 c.c. of ice-cold pyridine. Water precipitated a yellow oil, which became dark red, and finally changed to a purple slime which did not solidify; on dissolving this product in a small quantity of glacial acetic acid, which was then allowed to become diluted by exposure to air during several weeks, 2 grams of colourless crystals separated, melting at 134° after recrystallisation from alcohol.

0.4010 gave 24.4 c.c. nitrogen at 15° and 775 mm.  $N = 7.27$ .

$C_{24}H_{24}O_4N_2$  requires  $N = 6.93$  per cent.

It is very soluble in hot alcohol, from which it separates in needles, and moderately soluble in boiling petroleum, which deposits hard nodules. A solution containing 0.6897 gram in 25 c.c. of chloroform at 21° gave  $\alpha_D$  2°51' in a 2-dcm. tube, whence  $[\alpha]_D + 51.6^\circ$ .

The remarkable aspect of this compound is its behaviour on hydrolysis, coupled with the fact that it is produced when the  $\delta$ -dioxime also is submitted to the action of benzoyl chloride in pyridine. Although derivable, however, from both  $\beta$ - and  $\delta$ -dioximes, it yields neither on hydrolysis; alcoholic potassium hydroxide converted it into a compound which was scarcely soluble in ethyl acetate, and crystallised from alcohol in minute, silky needles infusible below 260°.

0.0953 gave 12.2 c.c. nitrogen at 19° and 755 mm.  $N = 14.62$ .

$C_{10}H_{16}O_2N_2$  requires  $N = 14.28$  per cent.

The substance therefore appears to have the composition of a dioxime, but it is distinguished from the four dioximes already known by the indifference of a solution in 2 per cent. sodium hydroxide towards ferrous sulphate.

#### *Benzoyl Derivatives of the $\gamma$ -Dioxime.*

*Monobenzoyl Derivative.*—The dioxime was dissolved in 5 parts of dry pyridine cooled by immersion in melting ice, and treated with one molecular proportion of benzoyl chloride; after an interval of 1 hour the product was mixed with water, which precipitated a colourless solid. This was insoluble in dilute sodium hydroxide, and after being washed with water until the odour of pyridine was no longer perceptible, it was recrystallised from absolute alcohol, in which it dissolves somewhat sparingly; large prismatic needles were deposited and melted at 172°, evolving gas.

0.2408 gave 20.0 c.c. nitrogen at 19° and 770 mm.  $N = 9.67$ .

$C_{17}H_{20}O_3N_2$  requires  $N = 9.33$  per cent.

A solution containing 0.5006 gram in 50 c.c. of chloroform at 20° gave  $\alpha_D^{24}$  in a 2-dcm. tube, whence  $[\alpha]_D + 20.0^\circ$ . It is insoluble in cold concentrated potassium hydroxide, but dissolves readily on warming. The substance is only moderately soluble in hot glacial acetic acid, from which it crystallises in small prisms; chloroform dissolves it sparingly, more than 50 c.c. being required by 1 gram.

*Action of Nitrous Acid.*—Twelve grams were suspended in 150 c.c. of glacial acetic acid, and treated with 4 grams of sodium nitrite, which was added in small quantities to the cold liquid. The benzoyl derivative slowly dissolved, and on diluting the pale brown liquid minute needles separated; the product crystallised from boiling alcohol in colourless prisms melting at 112°, and soon after evolving gas.

0.3469 gave 38.8 c.c. nitrogen at 21° and 770 mm.  $N = 12.90$ .

$C_{17}H_{19}O_4N_3$  requires  $N = 12.79$  per cent.

The solution in phenol develops a deep green coloration with concentrated sulphuric acid on warming, the diluted liquid becoming intense dark green when treated with alkali. The substance dissolves slowly in cold potassium hydroxide, forming a pale brown solution which contains nitrite.

*Dibenzoyl Derivative.*—Benzoyl chloride (2 mols.) was added to the dioxime dissolved in 5 parts of cooled pyridine, the liquid becoming quickly filled with crystals of the hydrochloride. The colourless product obtained on diluting the pyridine with water was washed, and dried in air, the yield, as in the case of the foregoing substance, being quantitative. The substance was recrystallised from boiling alcohol, from which it separated in well-formed, refractive prisms melting at 159°. It is insoluble in hot aqueous potassium hydroxide.

0.3076 gave 18.6 c.c. nitrogen at 20° and 770 mm.  $N = 7.00$ .

$C_{24}H_{24}O_4N_2$  requires  $N = 6.93$  per cent.

A solution containing 0.3514 gram in 25 c.c. of chloroform at 20° gave  $\alpha_D - 12'$  in a 2-dcm. tube, whence  $[\alpha]_D - 7.1^\circ$ .

An attempt which was made to half-hydrolyse the dibenzoyl derivative led only to the  $\gamma$ -dioxime, no monobenzoyl derivative being isolated. An alcoholic solution containing 7.6 grams of the dibenzoyl compound was treated with small quantities of alcohol in which 0.45 gram (1 mol.) of sodium had been dissolved, the solution developing an intense yellow coloration which disappeared on shaking. After heating during half an hour, the alcohol was evaporated, and the residue, which contained ethyl benzoate, was mixed with water and

shaken with ether, the residue from which, when hydrolysed with alcoholic sodium hydroxide, gave no precipitate with carbon dioxide. The aqueous extract of the product from the main hydrolysis was freed from ether and saturated with carbon dioxide, which precipitated 1.5 grams of a colourless substance readily soluble in boiling water, from which it crystallised in lustrous, silky needles melting at  $138^{\circ}$ .

0.1796 gave 22.4 c.c. nitrogen at  $22^{\circ}$  and 769 mm.  $N = 14.32$ .

$C_{10}H_{16}O_2N_2$  requires  $N = 14.28$  per cent.

The product of the hydrolysis of the dibenzoyl derivative is, therefore, the  $\gamma$ -dioxime, which has thus been obtained more highly purified than on previous occasions. Doubtless, the necessity of using mineral acid and of recrystallising from a large quantity of boiling water is responsible for the low melting point of the specimen described before, since the  $\gamma$ -dioxime is readily changed into the  $\delta$ -modification (Trans., 1903, 83, 520). Although the melting point of the purified substance is  $138^{\circ}$  instead of  $135^{\circ}$ , the statement of the specific rotatory power (*loc. cit.*) requires no modification.

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## XCI.—*The Vapour Density of Hydrazine Hydrate.*

By ALEXANDER SCOTT.

IN an important paper on the preparation and properties of hydrazine hydrate and the halogen salts of diammonium, Curtius and Schultz (*J. pr. Chem.*, 1890, 42, 521) record a number of determinations of the vapour density of the hydrate made at various temperatures both by Hofmann's and by V. Meyer's methods.

The conclusions they arrived at are :

1. The molecular weight of the hydrate as determined in a vacuum at  $100^{\circ}$  is  $50 = N_2H_4 \cdot H_2O$ .
2. At  $170^{\circ}$  under the ordinary pressure, the molecular weight corresponds with half that at  $100^{\circ}$  in a vacuum, showing that the hydrate is completely dissociated into hydrazine and water.
3. At higher temperatures, the molecular weight increases, although at  $300$ — $400^{\circ}$  it does not again reach 50.
4. In a lead bath, the vapour density determined is so high as to indicate a molecular weight approximately double that at  $100^{\circ}$  in a vacuum, that is,  $100 = 2(N_2H_4 \cdot H_2O)$  or  $N_4H_{12}O_2$ .

These conclusions are very remarkable, and, if true, indicate that hydrazine and water are completely combined in the state of vapour at  $100^{\circ}$ , but are completely dissociated at  $170^{\circ}$ , and that at still higher temperatures these substances recombine to form molecules still more complex than those existing at  $100^{\circ}$ .

The want of any details of manipulation renders it impossible to criticise the methods employed in the determinations; for example, it is not stated what gas was contained in V. Meyer's apparatus, and, as might be expected, this is a point of great importance. The only explanation which suggested itself was that there must be some errors of observation: this seemed all the more probable as the results given are far from being concordant. Having some very pure hydrazine hydrate which agreed in its boiling point and composition, as determined by titration, with that described by Curtius and Schultz, it was decided to redetermine the vapour density at various temperatures. As will be seen, the results are entirely opposed to those obtained by Curtius and Schultz.

The sample of hydrazine hydrate employed boiled at  $119.5^{\circ}$  under 765 mm. pressure and contained 64 per cent. of hydrazine.

The vapour densities required by theory are: 25 for  $(N_2H_4, H_2O)$ , 12.5 for  $N_2H_4 + H_2O$ , 9.375 for  $N_2 + 4NH_3 + 3H_2O$ , from the decomposition of  $3(N_2H_4, H_2O)$ , and still lower values would be obtained if the temperature were high enough to decompose the ammonia into hydrogen and nitrogen.

#### *A. Experiments by Hofmann's Method.*

- I. 0.0670 gave 133.8 c.c. at 366 mm. and  $98.8^{\circ}$ . V. D. = 15.82.  
 II. 0.0672 gave 134.5 c.c. at 367.4 mm. and  $98.8^{\circ}$ . V. D. = 15.71.

In the second experiment the temperature was raised by means of xylene vapour, when the volume increased to 155.4 c.c. at  $442.6$  mm. and  $138^{\circ}$ . V. D. = 12.48.

After cooling down and then reheating in steam, the value for the vapour density was found to be 15.71, a value identical with that obtained before heating in xylene vapour.

#### *B. Experiments by V. Meyer's Method.*

(In xylene vapour ( $138^{\circ}$ ) with air in apparatus.)

- I. 0.0468 gave 45.8 c.c. at 744.1 mm. and  $20.2^{\circ}$ . V. D. = 12.50.  
 II. 0.0475 gave 46.1 c.c. at 744.6 mm. and  $20.4^{\circ}$ . V. D. = 12.61.

(In aniline vapour ( $183^{\circ}$ ), air in apparatus.)

- III. 0.0476 gave 49.1 c.c. at 743.2 mm. and  $20.8^{\circ}$ . V. D. = 11.91.  
 IV. 0.0347 gave 39.75 c.c. at 739.3 mm. and  $20.8^{\circ}$ . V. D. = 10.78.  
 V. 0.0361 gave 41.95 c.c. at 737.2 mm. and  $21.4^{\circ}$ . V. D. = 10.68.

In all three experiments the expelled air was given off slowly towards the end, suggesting some slow chemical change.

(In aniline vapour ( $183^{\circ}$ ), nitrogen in apparatus.)

VI. 0.0360 gave 39.0 c.c. at 732.3 mm. and  $21.6^{\circ}$ . V. D. = 11.54.

VII. 0.0354 gave 37.85 c.c. at 739.3 mm. and  $19.8^{\circ}$ . V. D. = 11.51.

These determinations show that at  $183^{\circ}$  the hydrazine is beginning to decompose and to be oxidised by the oxygen of the air.

The following determinations were made in an apparatus of Jena glass at a temperature of about  $480^{\circ}$ , obtained by means of a Meyer's hot-air bath and determined by means of a Callendar and Griffith's resistance thermometer. In each case, nitrogen was used to fill the apparatus.

VIII. 0.0320 gave 38.7 c.c. at 748.8 mm. and  $16^{\circ}$  (bath at  $466^{\circ}$ ).  
V. D. = 9.92.

IX. 0.0339 gave 44.9 c.c. at 748.8 mm. and  $16^{\circ}$  (bath at  $483^{\circ}$ ).  
V. D. = 9.05.

X. 0.0320 gave 40.9 c.c. at 748.8 mm. and  $16^{\circ}$  (bath at  $482^{\circ}$ ).  
V. D. = 9.38.

XI. 0.0250 gave 33.5 c.c. at 748.3 mm. and  $16^{\circ}$  (bath at  $482^{\circ}$ ).  
V. D. = 8.96.

These determinations indicate that the ammonia produced by the decomposition of the hydrazine is, in turn, decomposed to a certain extent into nitrogen and hydrogen. As was expected, there is not the slightest indication of any formation of larger molecules, but quite the reverse.

*C. Experiments with Lumsden's Apparatus* (Trans., 1903, 83, 342).

(Air in apparatus. Volume = 133.7 c.c.)

I. 0.0221 gram, temp.  $138.3^{\circ}$ , increase of pressure = 206.8 mm.  
V. D. = 10.11.

II. 0.0221 gram, temp.  $138.3^{\circ}$ , increase of pressure = 219.2 mm.  
V. D. = 9.6.

In both experiments, the pressure towards the end increased very slowly, and the maximum reading was taken.

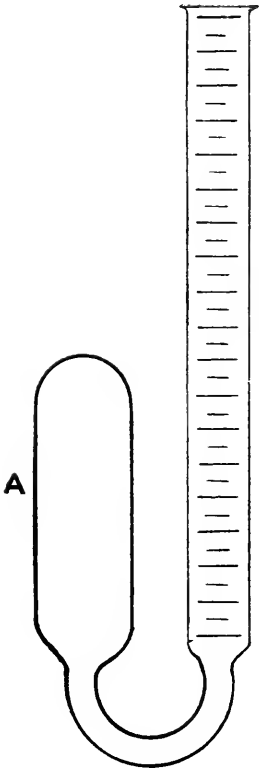
(Nitrogen in apparatus.)

III. 0.0235 gram, temp.  $138.6^{\circ}$ , increase of pressure = 180 mm.  
V. D. = 12.44.

IV. 0.0223g ram, temp.  $138.6^{\circ}$ , increase of pressure = 170.2 mm.  
V. D. = 12.48.

- V. 0.0223 gram, temp.  $183.2^{\circ}$ , increase of pressure = 191.2 mm.  
V. D. = 12.32.
- VI. 0.0200 gram, temp.  $182.4^{\circ}$ , increase of pressure = 171.6 mm.  
V. D. = 12.29.
- VII. 0.0195 gram, temp.  $299^{\circ}$ , increase of pressure = 251.5 mm.  
V. D. = 10.27.
- VIII. 0.0166 gram, temp.  $299.6^{\circ}$ , increase of pressure = 221.9 mm.  
V. D. = 9.92.

Two determinations were made by a modification of V. Meyer's method with fusible metal; the actual form of the apparatus employed was that shown in the figure.



The diameter of the bulb A, in which the hydrate was vaporised, was about 25 mm. and that of B about 18 mm. The tube B, which was about 230 mm. in length, was graduated in millimetres and carefully calibrated. A weighed quantity of the hydrate having been introduced into A in a tiny stoppered tube, the whole was raised to the temperature desired. The volume of vapour was determined from the readings on B before and after vaporisation, and the pressure from the difference between the levels of the fusible metal in A and B and reduced to mercury pressures (by multiplying by 0.705 the specific gravity of the fusible metal: mercury = 1.0).

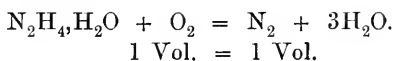
After the substance had been introduced and vaporised, the temperature of the apparatus was raised to  $300^{\circ}$  and kept at this for 20 hours, then allowed to cool somewhat and placed in a glycerin bath carefully adjusted to  $150^{\circ}$ . In the first experiment, it was found that 0.0194 gram gave 31.8 c.c. of gas at  $150^{\circ}$  and 821 mm. pressure, giving V. D. = 9.77.

In a second experiment, 0.0178 gram gave 30.2 c.c. of gas at  $150^{\circ}$  and 788 mm. pressure, giving V. D. = 9.83.

The gas remaining after the apparatus had cooled was found to be nitrogen, the volume of which in the second experiment was found to

be 3.4 c.c. at 709 mm. and 16°, corresponding with 0.0037 gram, the theory for complete decomposition into nitrogen, ammonia, and water being 0.0033.

In order to test the behaviour of hydrazine hydrate with air at high temperatures, about 0.05 gram was put into a vapour density bottle and sealed up in a tube containing about 100 c.c. of air under the ordinary atmospheric pressure. After heating for 6 hours to 150—160°, it was allowed to cool and then opened under water. The enclosed gas was under atmospheric pressure, and when tested was found to contain no free oxygen. This would be explained on the assumption that the following change took place:



About 0.1 gram was heated similarly at 300° in an atmosphere of nitrogen for 6 hours, and after cooling it was found that the pressure was notably above that of the atmosphere, and the escaping gas smelt of ammonia, the equation  $3\text{N}_2\text{H}_4 = 4\text{NH}_3 + \text{N}_2$  probably representing the change which took place; some hydrazine, however, remained undecomposed.

A similar experiment was made by heating some hydrazine hydrate in a vacuum at 300° for 12 hours. A weighed quantity (0.567 gram) was introduced into the large tube by taking a small bulb on a capillary tube, sealing up one end, and closing the other with fusible metal. The products of the decomposition were passed through a weighed (exhausted) apparatus consisting of (1) a dry caustic soda tube, (2) a sulphuric acid tube, and the escaping gas measured.

The gain of the caustic soda tube	=	0.5251
"      "      " sulphuric acid "	=	0.0246
Weight of nitrogen	=	0.0142
		<hr/>
Total	=	0.5639
Weight of hydrate taken	=	0.5668

The gas was pure nitrogen, but the gain in the caustic soda tube was due to undecomposed hydrate as well as to the water formed, which no doubt retained some of the ammonia, which it was hoped might be almost all caught by the sulphuric acid. The weight of ammonia ought to have been 0.0345.

A similar experiment was made, but instead of collecting the gases by a Sprengel pump the tube was opened under boiled water and the solution titrated. The hydrazine was not all decomposed by heating at 300° for 6 hours, the amount of acid employed being almost exactly

that which would be required to neutralise the ammonia corresponding with the nitrogen obtained.

The weights of hydrazine taken and nitrogen obtained were 0.1182 and 0.0174 respectively, whereas complete decomposition requires 0.0221.

The volume of *N*/10 acid required was 25.4 c.c., the amount calculated for complete decomposition being 31.5 c.c. 0.0174 nitrogen corresponds with 0.0423 ammonia, which requires 25.0 c.c. *N*/10 acid.

A determination by Dumas' method in boiling diphenylamine (295°) gave *V. D.* = 12.2; this, as well as the very small amount of nitrogen left on admitting water to the bulb, show that when the vapour is undiluted the secondary decomposition even at this high temperature is slight.

These experiments prove:

1. That at 100° in a vacuum, hydrazine hydrate in vapour is dissociated into hydrazine and water to the extent of 58 per cent., and that at 140° this dissociation is complete.

2. That at 183° under ordinary atmospheric pressure a further change takes place, namely, the decomposition of hydrazine into nitrogen and ammonia.

3. That at 460—480°, not only is this further change completed, but the ammonia itself begins to decompose.

4. That at 183° the oxygen of the air attacks the hydrazine, especially when under somewhat increased pressure, although under similar pressures in an atmosphere of nitrogen, hydrazine seems to be stable in presence of water, but not at 300°.

The initial temperature and the rate of the decomposition seem to be considerably influenced by the nature of the surfaces to which the hydrazine vapour is exposed, as well as by its dilution with other gases.

I have much pleasure in acknowledging the assistance I have received in this work from the manipulative skill of Mr. J. D. Kettle, B.Sc., and Mr. W. Green, assistants in the Davy Faraday Laboratory.

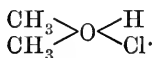
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XCII.—*The Basic Properties of Oxygen. Additive Compounds of the Halogen Acids and Organic Substances and the Higher Valencies of Oxygen. Asymmetric Oxygen.*

By EBENEZER HENRY ARCHIBALD and DOUGLAS MCINTOSH.

*Introduction.*

THE possible quadrivalency of oxygen was suggested as early as 1864 by Naquet (*Compt. rend.*, 1864, 58, 381, 675), from the analogy of oxygen to sulphur, tellurium, and selenium, all of which act as quadrivalent elements, but it was not until 1875 that Friedel (*Bull. Soc. chim.*, 1875, [ii], 24, 166, 241) demonstrated the existence of methyl ether hydrochloride, a substance containing quadrivalent oxygen, to which Wurtz gave the constitution



Friedel came to the conclusion that in this case the oxygen was quadrivalent, and that the valency depended on the temperature, as well as on the radicles forming the compounds. Van't Hoff (*Ansichten über organ. Chem.*) compared oxygen and sulphur compounds, and remarked that in these elements two bonds are prominent. In sulphur, the first two are negative, whilst the third and fourth, although weaker, are positive and give to sulphur its basic nature, and that this analogy may be extended to the oxygen compounds, methyl ether, and ethyl alcohol. In these substances, two of the oxygen linkings are positive, and hence compounds with the chlorides of the less basic metals are possible.

Baeyer and Fischer (*Annalen*, 1876, 183, 27, 68) prepared and analysed additive compounds of fluorescein and sulphuric acid, and of orcinphthalein and hydrogen chloride; Dale and Schorlemmer (*Annalen*, 1879, 196, 84) prepared compounds of aurin with acids; Wallach (*Annalen*, 1888, 246, 281) combined cineol with the halogen hydrides, and Perkin (*Trans.*, 1896, 69, 1439) obtained similar derivatives of pyrone. These investigators have explained their results on the old valency theory, but it is obvious that a simpler explanation is possible, based on the higher valency of oxygen.

This explanation was given by Collie and Tickle (*Trans.*, 1899, 75, 710) in their work on the additive compounds of dimethylpyrone with various acids. They referred the compounds isolated to a hypothetical

base,  $\text{H}_3\text{:O}\cdot\text{OH}$ , the existence of the ethyl derivative,  $\text{C}_2\text{H}_5\cdot\text{H}_2\overset{\text{IV}}{\text{O}}\cdot\text{OH}$ , of which is indicated by Kohlrausch's conductivity measurements of mixtures of ethyl alcohol and water.

Collie and Tickle remark that compounds of this nature, in which the third and fourth bonds are weak, are doubtless difficult to obtain, whilst Baeyer and Villiger (*Ber.*, 1901, 34, 2679, 3612; 1902, 35, 1201) show that these bonds are not necessarily weak, and that such compounds may be easily prepared if the proper acids are used. They also emphasise the fact that these compounds contain quadrivalent oxygen, and give to compounds of ketones and acids the constitution  $\text{>C:O<}\overset{\text{H}}{\underset{\text{X}}{\text{N}}}$ , instead of that usually assigned to them.

Baeyer and Villiger, who have made an exhaustive study of substances which may contain quadrivalent oxygen, have isolated and examined compounds of ethers, alcohols, acids, esters, aldehydes, and ketones with oxalic, ferrocyanic, ferricyanic, cobalticyanic, phospho-wolframic, platinocyanic, and chloroplatinic acids, and have in all cases satisfactorily explained their results by assuming that the oxygen is quadrivalent.

From the physico-chemical standpoint, Brühl (*Ber.*, 1895, 28, 2847, 2866) and Walden (*Ber.*, 1901, 34, 4185; 1902, 35, 1764) have pointed out that in water and hydrogen peroxide the oxygen is probably quadrivalent, while Kablukoff (*Zeit. physikal. Chem.*, 1889, 4, 429) and Jüttner (*Zeit. physikal. Chem.*, 1901, 38, 56) have shown that, with certain acids, alcohols and ethers give rise to compounds which have properties usually associated with salts.\*

In a recent paper (Walker, Archibald, and McIntosh, *Proc.*, 1904, 20, 134), it has been shown that many organic substances containing oxygen or nitrogen dissolve in the liquefied halogen hydrides to form conducting solutions,† and that there is strong evidence in support of the formation of additive compounds. This could be satisfactorily explained in the case of the trivalent nitrogen compounds by assuming that the nitrogen changed to the quinquevalent form, and a similar explanation could be given for oxygen. In this paper, we shall discuss only three classes of oxygen compounds, namely, the ketones, the ethers, and the alcohols, although the paper previously cited shows that compounds are doubtless formed with the esters, the aldehydes, and some acids; the constitution of the various products

\* We have referred only to some of the more important papers. For a full account, see Schmidt, "Ueber die basischen Eigenschaften des Sauerstoffes."

† A large number of quantitative conductivity determinations have been made by us in conjunction with B. D. Steele, and will be published later. The molecular conductivity invariably decreases with dilution, pointing to the formation of compounds in solution.

will be explained by assuming that oxygen possesses valencies higher than those usually assigned to it.

*The Basic Properties of Oxygen.\**

We have obtained definite compounds of hydrogen iodide with ethyl ether, methyl amyl ether, and phenyl methyl ether, with acetone, and with ethyl and propyl alcohols.

Similar compounds were obtained with hydrogen bromide, excepting in the case of ethyl alcohol, and with hydrogen chloride, excepting with the two alcohols. All these compounds were colourless, crystalline substances having sharp melting points, which in nearly all cases were well above the melting points of the reacting substances. These additive compounds readily formed supersaturated solutions in the acids from which they were prepared, and were easily precipitated from such solutions in the usual way, by the addition of a few crystals.

EXPERIMENTAL.

The acetone, ethers, and alcohols used in preparing these compounds were purified according to the usual methods, and in each case distilled at a practically constant temperature, which was that required for the pure liquid. In the case of the methyl ether, this temperature was about  $-22^{\circ}$ .

The acids, which were all made from pure materials, were dried by means of phosphoric oxide and condensed in a tube surrounded by a mixture of solid carbon dioxide and ether.

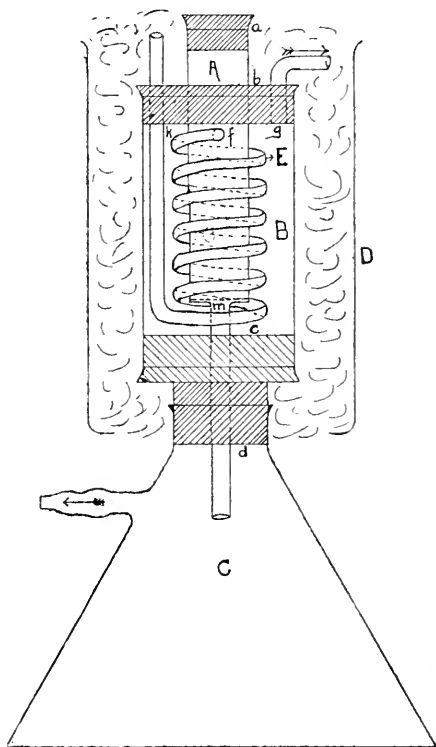
It was thought that we might obtain these additive compounds dry and suitable for analysis by filtering them on a porcelain filter plate covered with a layer of asbestos. If the salt was surrounded by a jacket containing a cooling mixture, at a temperature somewhat below the melting point of the compound, but still above the freezing point of either constituent, it would be possible to draw a current of cold air through the salt until it was dry.

Several methods of drying and weighing were tried before a satisfactory scheme was evolved. The figure on page 922 represents the apparatus which was finally adopted for drying the different compounds.

The filter tube, *A*, passes through the india-rubber stoppers, *b*, *c*, and *d*, into the filtering flask, *C*. The stoppers, *b* and *c*, fit tightly into the jacket tube, *B*, which contains a cooling mixture of solid carbon

\* We believe that the third and fourth bonds of oxygen are amphoteric, that is, slightly negative as well as positive, since ethers and alcohol give conducting solutions in liquid ammonia.

dioxide and ether. By connecting a suction pump to the tube *g*, which passes through *b*, the pressure over this mixture can be reduced sufficiently to lower the temperature to  $-103^{\circ}$ . A glass spiral surrounds the filter tube, one end passing up through the stopper at *k*, the other being sealed into the filter tube at *f*. By means of this arrangement, a current of cold dry air can be drawn through the substance to be dried, which rests on a mat of asbestos over the porcelain filter plate, *m*. The stopper, *a*, can be removed at any time and the



substance pressed down firmly on to the asbestos. A jacket of natural wool, held in place by the bottomless beaker, *D*, surrounds the whole and reduces the amount of heat conducted to *B*.

The cooling mixture in the jacket could be brought to the desired temperature either by adding more solid carbon dioxide and reducing the pressure over the mixture, or by adding more of the warm ether. An ordinary weighing bottle, used as a containing vessel in weighing out the compound, was cooled in liquid air and the weighing performed while the bottle was cold, and therefore covered with a very thin film

of ice, this being the condition under which the subsequent weighing would be made. Repeated weighings, in these circumstances, showed that the film of ice did not amount to more than a few milligrams, and as we seldom worked with less than two or three grams, the error due to this was quite inappreciable.

The additive compounds rapidly commenced to separate on adding the organic liquid, acetone, ether, or alcohol, previously cooled to a temperature of  $-80^{\circ}$ , to about 10 c.c. of the liquid hydrogen halide. The heat generated simultaneously, which was presumably due to the formation of the compound, was sufficient to cause slight explosions during the earlier stages of the mixing. When these explosions had almost ceased, that is, while an excess of acid still remained, the tube containing the compound and mother liquor was removed to a warmer bath and the compound allowed to go into solution in the excess of the halide. An excess of acid was chosen for the mother liquor, as the compounds appeared to be much more soluble in this solvent than in the other constituent. After solution had taken place, the mixture was again cooled and the compound allowed to crystallise until a sufficient quantity had separated, when the mixture was poured on to the filter and the salt dried by aspiration. A portion of the dry compound was then scooped out with a glass spoon which had been cooled in liquid air, transferred to the tared weighing bottle, which was surrounded by a cooling mixture, the bottle tightly stoppered, and weighed under comparable conditions. The bottle was then again cooled, immersed mouth downward in a beaker of water, the cork removed, and the water allowed to absorb the acid slowly. The acid solution was then titrated with standard barium hydroxide solution, and from the data obtained the percentage of acid in the compound was calculated.

In a few cases, the large heat effect produced on mixing substances such as acetone and liquid halide was made use of in determining the constitution of the product and in checking the gravimetric analysis, the evolution of heat serving as an indicator. The acid was titrated against a known volume or weight of acetone or alcohol, assuming that when the point was reached at which there was no further evolution of heat the acid had been completely neutralised. In some cases, where the product melted at a temperature far below the melting point of either constituent, this method of analysis was employed exclusively as being in this instance more trustworthy than a gravimetric process. Although we are quite aware of many objections which might be brought against this method, nevertheless, since concordant results were obtained by both methods, we think that considerable value should be attached to the results. In making one of these volumetric determinations, a quantity of the halogen halide was

measured out into a calibrated test-tube placed in a cooling mixture. A pycnometer filled with acetone or alcohol was weighed and cooled, and when both had reached a temperature of about  $-80^{\circ}$ , the acetone or alcohol was added drop by drop to the liquid halide until the explosions had entirely ceased. Another weighing of the pycnometer gave the amount of acetone or alcohol which had been added.

As this work was carried on during the winter months, when the outside temperature was often as low as  $-15^{\circ}$ , advantage was taken of this for the purpose of analysing those compounds the melting points of which were above  $-20^{\circ}$ . Such compounds were filtered and the weighings made out of doors.

With the exception of a few preliminary experiments made to test our analytical methods, we give the results of all our analyses.

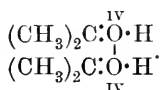
### *Acetone Compounds.*

The compound of acetone with hydrogen iodide was soluble both in acid and acetone and melted at  $-18^{\circ}$ , whilst the melting points of hydrogen iodide and acetone are  $-50^{\circ}$  and  $-96^{\circ}$  respectively. The analysis of different preparations gave the following results:

No. of preparation analysed.	Per cent. of acid found.	No. of preparation analysed.	Per cent. of acid found.
I	51.1	III	53.3
I	53.3	III	49.6
II	55.5		

$[(\text{CH}_3)_2\text{CO}]_2\text{HI}$  requires  $\text{HI} = 52.5$  per cent.

Assuming the oxygen to be quadrivalent, the structural formula for such a compound would be



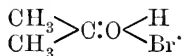
The compound of acetone with hydrogen bromide was even more stable than the preceding substance, melting at  $-9^{\circ}$ , whilst hydrogen bromide melts at  $-86^{\circ}$ . Two different preparations were analysed with the following results:

No. of preparation analysed.	Per cent. of acid found.	No. of preparation analysed.	Per cent. of acid found.
I	57.3	II	58.8
I	57.0	II	57.9

—  
Mean value = 57.8

$\text{CH}_3\cdot\text{CO}\cdot\text{CH}_3\cdot\text{HBr}$  requires  $\text{HBr} = 58.3$  per cent.

In this case, the structural formula on the above assumption would be



In order to ascertain if this compound were stable as a liquid, a sample was kept for twenty-four hours at  $-4^\circ$ . On analysis, a part was found to have decomposed, forming ethyl bromide, and only half the original amount of acid was present.

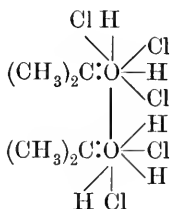
The compound formed from acetone and hydrogen chloride melts at about  $-85^\circ$ , whilst the melting point of the hydrogen chloride is about  $-112^\circ$ . Analysis of three different preparations of this substance gave the following results :

No. of preparation analysed.	Per cent. of acid found.	No. of preparation analysed.	Per cent. of acid found.
I	59.9	III	60.7
II	59.9	III	60.2
II	59.9		—

Mean value = 60.2

$(\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_3)_2, 5\text{HCl}$  requires  $\text{HCl} = 61.2$  per cent.

If we suppose that the lower temperature has raised the valency of the oxygen to 8, the constitution of this substance can be represented thus :



### *Ether Compounds.*

The compound of ethyl ether with hydrogen iodide resembled the acetone compound in many respects, but was not soluble in ether even when melted ; it melted at  $-18^\circ$ , whilst the melting point of solid ether is  $-117^\circ$ . Two different preparations were analysed with the following results :

No. of preparation ...	I	II	II	Mean.
Percentage of acid ...	60.4	62.4	59.7	60.7*

$(\text{C}_2\text{H}_5)_2\text{O}, \text{HI}$  requires  $\text{HI} = 63.4$  per cent.

\* Since the compound was washed with ethyl ether, the low value obtained may be due to the absorption of this liquid.

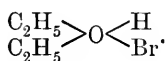
The structural formula for the above compound may be represented thus;  $\begin{array}{c} \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \end{array} > \text{O} < \begin{array}{c} \text{H} \\ \text{I} \end{array}$ , the oxygen being quadrivalent, or as  $\begin{array}{c} \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \end{array} > \text{O} : \text{I} \cdot \text{H}$ , assuming also that iodine is trivalent.

Experiments by Messinger and Engels (*Ber.*, 1888, 21, 326) have indicated the existence of a compound  $(\text{C}_4\text{H}_{10}\text{O})_2, \text{HI}$ . We have failed to obtain a crystalline compound of this nature and regard its existence as doubtful.

The melting point of the ether hydrogen bromide compound was  $-40^\circ$ . Two different preparations were analysed:

No. of preparation ...	I	II	II	Mean.
Percentage of acid ...	52.4	54.0	54.1	53.2
$\text{C}_4\text{H}_{10}\text{O}, \text{HBr}$ requires $\text{HBr} = 52.3$ per cent.				

The structural formula of this compound must be analogous to that of the previous compound and would be represented thus:



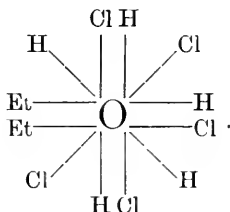
The compound formed from ether and hydrogen chloride melted at about  $-92^\circ$ .

Two analyses of a specimen were made with the following result: percentage of acid found = 71.3 and 71.8 (mean = 71.6).

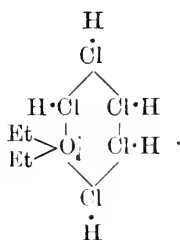
$\text{C}_4\text{H}_{10}\text{O}, 5\text{HCl}$  requires  $\text{HCl} = 71.2$  per cent.

We have also estimated the proportion of acid to ether in this compound by titration in the foregoing manner: 3.24 grams of ether neutralised 6.8 c.c. of acid, and as the latter had a sp. gr. 1.22 at the temperature of experiment, therefore the ether was neutralised by 8.30 grams of acid. The molecular proportion is therefore 1 part of ether to 5.19 of acid, which accords with the preceding estimation.

Assuming that at this low temperature the oxygen of the ether has ten unsatisfied bonds, we can represent the structure of the molecule thus:



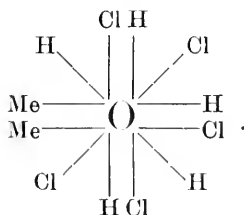
If chlorine is assumed to be tervalent, the formula might then be represented as follows :



It seemed of considerable interest to examine the compound formed from methyl ether and hydrogen chloride and described long ago by Friedel (*loc. cit.*). From analogy, the melting point of this substance would be below the melting point of hydrogen chloride and this was confirmed by subsequent experiment. By titrating, we found that one molecule of ether neutralised, in one experiment, 5.63, and in another, 4.58 molecules of acid. These results give respectively 81.6 and 78.4 per cent. of acid (mean value = 80.0 per cent.).

$\text{C}_2\text{H}_6\text{O} \sqrt{\text{HCl}}$  requires  $\text{HCl} = 80.0$  per cent.

In this, as in the case of the preceding compound, the structure of the molecule may be represented thus :



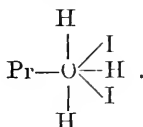
Friedel gave the composition of the compound as  $(\text{CH}_3)_2\text{O}, \text{HCl}$ , from the fact that a mixture corresponding roughly with this formula distilled at a constant temperature. If the distillation of a liquid of constant composition is looked on as the test of a compound, then solutions of hydrogen chloride, bromide, and iodide in water must be admitted to be compounds, which is directly opposed to Roscoe's conclusions. Furthermore, the molecular conductivity of such a mixture in the case of ethyl ether increases as the temperature diminishes, indicating that only a part of the ether and acid present have united to form a compound.

*Compounds with Alcohols.*

Hydrogen iodide and ethyl alcohol give a compound melting so low that it could not be analysed gravimetrically. Propyl alcohol gave a substance melting at about  $-65^{\circ}$ . Analyses of two different preparations of this compound gave the following results:

No. of preparation.....	1.	2.	3.	
Percentage of acid.....	78.1	80.5	80.5	mean = 79.7.
$C_3H_7 \cdot OH, 2HI$ requires $HI = 81.0$ per cent.				

If in the compound the oxygen is sexavalent, we can represent the structure of the molecule as follows:

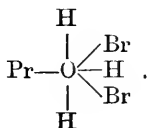


Some attempts were made to obtain the compound formed by the union of hydrogen iodide and amyl alcohol, but upon analysing the substance which separated out on cooling the following percentage values of the acid were found: 96.5, 101.5, and 100.5, showing that only hydrogen iodide had been precipitated.

With hydrogen bromide, propyl alcohol forms a compound which melts below the freezing point of the acid. The constitution of this substance was determined by titration. In one experiment, a molecule of propyl alcohol was neutralised by 1.945 molecules of acid; in another instance, a molecule of the alcohol was neutralised by 2.32 molecules of acid. The percentage values obtained for the two specimens would be 72.3 and 75.7 per cent. respectively.

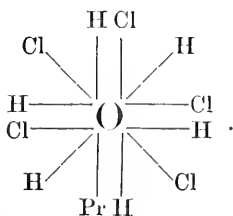
$C_3H_7 \cdot OH, 2HBr$  requires  $HBr = 73.0$  per cent.

The constitution of this compound, which must be analogous to that of the previous one, can be represented thus:



The compound of hydrogen chloride with propyl alcohol, like the preceding one with hydrogen bromide, had to be analysed by titration. In two cases, 1 molecule of alcohol was found to require 5.01 and 4.75 molecules of acid, the corresponding percentage values being 75.3 and 74.4;  $C_3H_7OH, 5HCl$  requires 75.2 per cent.  $HCl$ .

In this compound, the oxygen appears to have a valency of twelve, and the structural formula will therefore be :



In the various formulæ which have been given to represent the constitution of these compounds, we have assumed that oxygen possesses a valency ranging from four to twelve. The constitution could, however, be represented by means of quadrivalent oxygen only if we assume that the halogens were trivalent. On the former assumption, the formula of a typical compound, such as ethyl ether hydrobromide, would be  $\text{Et} > \text{O} < \begin{smallmatrix} \text{H} \\ \text{Br} \end{smallmatrix}$ , or, assuming that the bromine is trivalent, it would be represented by  $\text{Et} > \text{OH} : \text{Br} \cdot \text{H}$ .

Since these compounds in solution conduct the electric current according to Faraday's law, they must be ionised. In accordance with the first formula, the ether would probably move to the cathode, and according to the second to the anode. We have reason for believing that the first formula is the correct one.

### Collected Results.

	Molecules of acid.	Molecules of organic liquid.	Melting point.	Valency of oxygen.
HI .....	{ 1	Acetone (2)	- 18°	4
	{ 1	Ether (1)	18	4
	2	Alcohol (1)	70	6
HBr .....	{ 1	Acetone (1)	9	4
	{ 1	Ether (1)	40	4
	2	Alcohol (1)	85 (?)	6
HCl .....	5	Acetone (2)	85	8
	5	Ethyl ether (1)	92	12
	5	Methyl ether (1)	120 (?)	12
	5	Alcohol (1)	120 (?)	12

In the above table, we have collected our analytical results, and show the simplest proportions in which the compounds are formed and the temperatures at which they decompose (melt). If we suppose—an assumption not without objections—that chlorine, bromine, and iodine

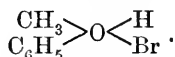
are monads,\* we have in the first two members, compounds with hydrogen iodide, which decompose at  $-18^{\circ}$ , the oxygen behaving as a quadrivalent element, whilst in the last, which decomposes at  $-70^{\circ}$ , the oxygen is a hexad.

In the hydrogen bromide compounds with ether and acetone, the decomposition point is relatively high and the oxygen is quadrivalent, but in the alcohol compound with a low melting point, the oxygen is sexavalent. In the case of hydrogen chloride, the melting points of the compounds are low and the oxygen has a valency of eight or twelve.

From these results, we conclude with Friedel that temperature is of importance in fixing the valencies of elements, a conclusion which seems in agreement with many molecular weight determinations made either by Meyer's method or by the cryoscopic process, and with the work of Ramsay and Shields on molecular complexity.

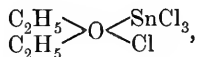
#### *Asymmetric Oxygen.*

We have prepared compounds of acids and mixed ethers by the foregoing method, and whilst these substances have not as yet been analysed, the constitution in the case of anisole is probably

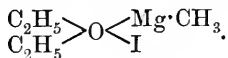


If this constitution is correct, the oxygen is in this case united to four different radicles and is asymmetric; it should therefore be possible to resolve the compound into its optically active constituents.

Further, compounds of the ethers with the weaker basic metals are known, such as



and doubtless a similar compound containing asymmetric oxygen could be formed from methyl ethyl ether analogous to the known compound,



These compounds are now under investigation.

In conclusion, we wish to express our thanks to Dr. B. J. Harrington and Dr. J. W. Walker for kindly interest shown during this work.

McDONALD CHEMISTRY BUILDING,  
MCGILL UNIVERSITY.

\* Steele and McIntosh have shown that bromine and iodine in hydrogen bromide and iodide are probably monads at low temperatures. Chlorine may act as a trivalent element.

XCIII.—*Limonene Nitrosocyanides.*

By WILLIAM AUGUSTUS TILDEN and FREDERICK PEACOCK LEACH.

It was shown by Wallach (*Annalen*, 1889, 252, 108) that when either *d*- or *l*-limonene is treated with an alkyl nitrite and hydrochloric acid, the resulting nitrosochloride consists of two isomeric compounds which are separable from each other by the use of chloroform and ether as solvents.

Limonene  $\alpha$ -nitrosochloride, which constitutes the greater part of the product, is the more soluble in these menstrua, and forms magnificent, transparent prisms, the melting point of which is stated by Wallach to be 103–104°, and having  $[\alpha]_D +$  or  $- 314^\circ$ , according as it is derived from *d*- or *l*-limonene (Conrady, *Annalen*, 1889, 252, 145).

Limonene  $\beta$ -nitrosochloride is much less soluble than the  $\alpha$ -compound; its melting point is rather uncertain, but is about 105–106°, and  $[\alpha]_D$  is approximately  $+$  or  $- 241^\circ$ . These compounds are regarded by Baeyer as being bimolecular with the formula  $(C_{10}H_{16}NOCl)_2$  (*Ber.*, 1895, 28, 648).

In a "Preliminary notice of some new derivatives of pinene and other terpenes" (*Proc.*, 1902, 18, 163), one of us, in conjunction with H. Burrows, referred to a nitrosocyanide obtained from crude limonene nitrosochloride by the action of potassium cyanide, which then appeared to be liquid; this compound has now been obtained as a well crystallised solid.

When the  $\beta$ -nitrosochloride prepared from *d*-limonene (orange oil) is digested at a temperature not exceeding 60° with an equivalent quantity of powdered potassium cyanide in the presence of 90 per cent. alcohol, the nitrosochloride gradually dissolves to a greenish-blue solution which ultimately becomes almost colourless. The product, when diluted with water, yields an oily precipitate, which after boiling, whereby a small portion of volatile liquid passes off, or after the lapse of a few hours, gradually assumes the form of a crystalline paste. The solid, drained from the liquid and recrystallised from light petroleum, forms transparent or opaque, colourless prisms which melt without decomposition at 90–91°. The same compound is formed when the crude nitrosochloride, that is, the mixture of  $\alpha$ - and  $\beta$ -varieties, is employed. On analysis the compound yielded 15.02 per cent. of nitrogen, whilst the formula  $C_{10}H_{16}NO \cdot CN$  requires 14.58.

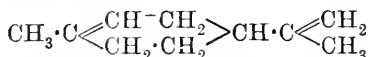
Limonene  $\beta$ -nitrosocyanide is easily soluble in alcohol, ether, benzene, chloroform, or hot light petroleum, but sparingly soluble in the cold solvent; it immediately decolorises bromine in chloroform solution. The compound is readily soluble in aqueous solutions of caustic alkalis, and is reprecipitated therefrom by acids.

After boiling with dilute sulphuric acid, the product reduces Fehling's solution. By the Schotten-Baumann process, a benzoyl derivative is readily formed, which crystallises from alcohol in pearly, lustrous plates melting at  $107^{\circ}$ . Analysis gave 9.55 per cent. of nitrogen, the formula  $C_{10}H_{15}NO \cdot CN \cdot C_7H_5O$  requiring 9.46 per cent. This benzoyl derivative is readily hydrolysed by alcoholic potash, yielding benzoic acid and the original substance. Limonene  $\beta$ -nitroso-cyanide is optically active, like the nitrosochloride, having  $[\alpha]_D + 165^{\circ}$  in benzene.

A methyl ether prepared by the action of methyl iodide and either alcoholic soda or silver oxide could only be obtained in the form of a viscid oil.

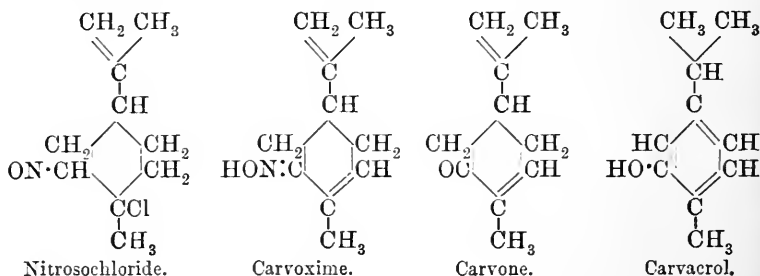
Determinations of molecular weight by the freezing point method gave somewhat anomalous results. In benzene, the highest value obtained was 168.7, but in naphthalene the value found was 191.6, which is practically identical with 192, the molecular weight represented by the simple formula  $C_{10}H_{16}NO \cdot CN$ .

The properties and reactions described are those of an unsaturated oxime, and since the formula,



for limonene has recently been established by Perkin (this vol., p. 654), it appears certain that the addition of the elements of nitrosyl chloride and the corresponding cyanide occurs in the ring. Moreover, the halogen goes to the tertiary carbon, while the nitroso-group necessarily attaches itself to the adjacent atom of carbon which supplies the requisite atom of hydrogen. Now when limonene nitrosochloride is deprived of the elements of hydrogen chloride, carboxime results, and this oxime has been produced directly by the interaction of carvone and hydroxylamine (Goldschmidt, *Ber.*, 1884, 17, 1577).

Hence carboxime and carvone must have the same structure, and are derived from limonene in the manner shown by the following diagram, which also indicates the relationship of the accepted formula for carvacrol.



The nitrosocyanide contains the CN group in the same position as the chlorine of the nitrosochloride. On boiling with alcoholic potash, ammonia was slowly evolved, and after several days the product, when mixed with water, gave no precipitate until neutralised by acid, when an oily precipitate was formed. A crystalline compound (m. p.  $130^{\circ}$ ) soluble in weak alkali was ultimately extracted from this substance, but whether it is the corresponding acid or not remains to be determined.

When pure  $\alpha$ -nitrosochloride from *d*-limonene was digested with alcohol and potassium cyanide, the corresponding cyanide was not isolated so readily. A semi-solid product was obtained from which a crystalline substance was extracted, which proved to be carvoxime (m. p.  $72^{\circ}$ ); analysis gave 8.84 per cent. of nitrogen, whilst the formula  $C_{10}H_{14}:NOH$  requires 8.45. The viscid products have not yet been made to yield a crystalline nitrosocyanide, but by treating them with benzoyl chloride and caustic soda a benzoyl derivative has been separated which has the same melting point as the benzoyl compound formed from the  $\beta$ -nitrosochloride. On analysis, it yielded 9.95 per cent. of nitrogen, which agrees closely with theory.

Wallach has traced the relations of some of the nitrolamines derived from the two nitrosochlorides, and finds that the derivatives of the  $\alpha$ -compound are identical with those of the  $\beta$ -compound (*Annalen*, 1889, 252, 113). Whether the cyanides derived from the  $\alpha$ - and  $\beta$ -nitrosochlorides are chemically different or identical remains to be determined.

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## XCIV.—*Estimation of Hydroxyl Groups in Carbon Compounds.*

By HAROLD HIBBERT and JOHN JOSEPH SUDBOROUGH.

TSCHUGAEFF (*Ber.*, 1902, 35, 3912) has described a process for detecting hydroxyl radicles in carbon compounds by the aid of Grignard's magnesium methyl iodide, the basis of the method being the determination of the amount of methane evolved when dry ethereal solutions of the hydroxyl derivative and Grignard's compounds are mixed. The reaction proceeds according to the equation  $R\cdot OH + CH_3\cdot MgI = R\cdot O\cdot MgI + CH_4$ , and the methane is collected in a Knop's nitrometer. It is stated that the volume of gas usually approximates to that

required by theory, although the method is not recommended for quantitative purposes.

In our examination of the red compounds formed by the union of *s*-trinitrobenzene with arylamines (Trans., 1901, 79, 522; 1903, 83, 1334), we wished to use some simple method for detecting and estimating hydroxyl radicles. In experimenting with Tschugaeff's method, we have found that quantitative results cannot be obtained owing to three following sources of error: (1) When a Knop's nitrometer with india-rubber connections is used, the water slowly permeates this material and reacts with the Grignard reagent, evolving methane. (2) When the reaction is conducted in a vessel filled with ordinary air, slow absorption of the oxygen by the magnesium methyl iodide occurs (compare Bouveault, *Bull. Soc. chim.*, 1903, 29, 1051). (3) When ether is employed as solvent, slight alterations in temperature produce considerable variations in the volume, owing to the change in the vapour pressure of the liquid.

We have overcome these difficulties by working in an atmosphere of dry nitrogen in place of ordinary air, using amyl ether as solvent and collecting the gas over dry mercury in a Lunge nitrometer or Hempel burette.

We first attempted to use toluene as a solvent, but found that in this medium, magnesium does not react with methyl iodide. A combination could not be detected even on boiling, but the addition of a little dry ether (5 c.c.) caused a slight reaction which became brisker as more of the liquid was introduced.

Blaise (*Compt. rend.*, 1901, 132, 839) states that the magnesium alkyl haloids are only formed in the presence of ether, and that this substance plays an important chemical part in the reaction. Our experiments indicate that other ethers may be employed in place of ethyl ether and that the reaction depends to a considerable extent on the presence of the C·O·C group in the molecule of the solvent.\*

#### *Preparation of the Magnesium Methyl Iodide Solution.*

The amyl ether employed was dried over calcium chloride, boiled for several hours with metallic sodium, treated with a small amount (5 c.c.) of the amyl ether solution of magnesium methyl iodide, and again boiled with sodium, then left for several hours over phosphoric oxide, and finally distilled.

Dry magnesium turnings (6·09 grams) were added to 100 c.c. of the dry ether, and 35·5 grams of methyl iodide dissolved in 20 c.c. of the ether were then introduced. The reaction which began when the

\* Tschelinzeff (*Ber.*, 1904, 37, 2084) has since shown that dimethylaniline may be substituted for ether.

mixture was gently warmed on the sand-bath was allowed to proceed at the ordinary temperature, and finally completed by heating the mixture for about half an hour. As a rule some 13—14 per cent. of the magnesium was not dissolved and the clear solution was decanted from this residue and made up to 200 c.c. with pure amyl ether. The solution should be kept out of contact with the atmosphere as far as possible because it absorbs moisture, oxygen, and carbon dioxide.

*Estimation of Hydroxyl Radicles.*

A stout flask of about 200 c.c. capacity is fitted with a doubly bored india-rubber stopper, which carries a stopcock reaching nearly to the bottom of the flask, and a short tube which is fitted by means of a length of thick-walled india-rubber tubing to a Lunge nitrometer or Hempel burette filled with dry mercury. Dry amyl ether (10—20 c.c.) and 0.10—0.25 gram of the substance are placed in the flask and an excess—about 15 c.c.—of the amyl ether solution of magnesium methyl iodide is placed in a small tube, which is lowered into the flask in a vertical position. The air in the flask is displaced by dry nitrogen, the flask is then attached to a Hempel burette filled with dry mercury and the apparatus left for 2 to 4 hours to attain a constant temperature. The height of the mercury, the temperature, and pressure are noted, and after mixing the two solutions and shaking vigorously, the level of the mercury is adjusted and the volume read off with the usual precautions.

A blank experiment was made in order to show that no gas is evolved when the magnesium methyl iodide solution is mixed with dry amyl ether. The flask was then heated in a glycerol bath first for 10 minutes at 120°, and then for 10 minutes at 140°. A small amount of white solid separated but there was no change in the volume of the gas.

The following hydroxyl derivatives have been used:— $\alpha$ - and  $\beta$ -naphthols, resorcinol, acetoxime, chloral hydrate, ethyl salicylate, pyrogallol, quinol, deoxybenzoin, benzoin, ethyl acetoacetate, and *o*-nitrophenol: the results obtained are tabulated on p. 936.

In addition to these compounds, we have experimented with two ketonic substances, namely, benzophenone and benzil, which do not contain hydroxyl groups and which cannot react in a tautomeric enolic form. In the former case, the results obtained were entirely negative; with benzil, on the other hand, a small amount (some 6 c.c. from 0.26 gram of the ketone) of gas was evolved, the origin of which we are not able to explain.

*Notes on the Experiments.*

Nos. 1, 2, and 3. The naphthols and their magnesium derivatives dissolved readily in cold amyl ether.

Nos. 4, 5, 6, and 7. Resorcinol, acetoxime, chloral hydrate, and ethyl salicylate dissolved readily in cold amyl ether. When the solutions were mixed with the magnesium methyl iodide a small amount of white precipitate was obtained in the case of resorcinol and acetoxime.

No. of expt.	Substance.	Weight.	Vol. of gas in c.c.	Temp.	Pressure in mm.	Vol. at N.T.P.	Theory.
1	$\alpha$ -Naphthol.....	0.2322	36.2	9°	756.5	34.9	36.0
2	".....	0.2665	42.4	9	754	40.7	41.3
3	$\beta$ -Naphthol.....	0.2239	36.0	10	751	34.3	34.7
4	Resorcinol .....	0.1852	78.6	9.3	751.6	75.2	75.2
5	Acetoxime .....	0.1301	41.1	9	759	39.7	39.8
6	Chloral hydrate .....	0.1440	40.9	9.2	763	39.7	38.8
7	Ethyl salicylate .....	0.2792	37.8	11	776	37.1	37.5
8	Pyrogallol .....	0.1264	69.8	9	757	67.3	67.2
9	Quinol .....	0.1190	51.5	12	768	49.9	48.3
10	Deoxybenzoin .....	0.2757	4.45	9.4	737	4.2	31.4
11	".....	0.3000	3.45	9	761	3.3	34.2
12	".....	0.2804	4.78	13.6	756.2	4.5	32.0
13	Benzoin .....	0.2814	31.9	14	762.4	30.5	29.6
14	Ethyl acetoacetate...	0.2290	37.3	11.3	767.2	36.1	39.3
15	".....	0.2150	35.7	11.3	762	34.4	36.9
16	<i>o</i> -Nitrophenol .....	0.1980	38.1	11.3	762	36.7	31.8

\* The vapour pressure of the amyl ether has been neglected in all the experiments.

No. 8. Pyrogallol itself dissolved readily in the ether, but the addition of the magnesium methyl iodide solution produced a copious white precipitate.

No. 9. Quinol was sparingly soluble in cold amyl ether, but dissolved readily on warming. In this experiment, when the reading had been taken before mixing, the flask and its contents were heated to 120° in a glycerol bath until the hydroxy-compound was dissolved; the two solutions were mixed, thoroughly shaken, kept at 120° for 20 minutes, and then allowed to cool and the volume ascertained. The heating was repeated, but no further increase occurred.

Nos. 10, 11, 12, 14, and 15. These experiments are interesting, as

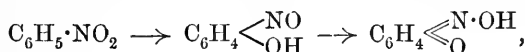
they deal with ketonic compounds which are capable of reacting in their enolic tautomeric forms. The results obtained indicate the enolising action of Grignard's reagent, the effect being more marked in the case of ethyl acetoacetate, which, according to W. H. Perkin (Trans., 1892, 61, 808), consists almost entirely of the ketonic form, and yet reacts in this case as if it were almost entirely in the enolic form. It follows from these results that this method is useless for the investigation of tautomeric substances of the keto-enolic type.

A fourth experiment conducted with deoxybenzoin gave a somewhat lower result, namely 1.2 c.c. of gas from 0.2882 gram.

No. 13. The benzoin was only sparingly soluble in amyl ether in the cold, and therefore, when the first reading had been taken, the flask was heated to about  $120^{\circ}$  in order to dissolve the benzoin, and after cooling somewhat, the two solutions were mixed, heated for 20 minutes at  $120^{\circ}$ , allowed to cool, and the volume of gas read off.

No. 16. When the two solutions were mixed, a reddish-brown precipitate was obtained, and a gas was evolved; the latter, after 4 hours at the ordinary temperature, amounting to 38.1 c.c.; this quantity is greater than that required for one hydroxyl group. When left for another 8 hours at the ordinary temperature, an additional 5 c.c. of gas were evolved, and after heating at  $115-120^{\circ}$  for 20 minutes, there was a further increase of 13 c.c., making a total of 56.1 c.c. The high results obtained with *o*-nitrophenol appears to be due to the presence of the nitro-group, as other nitro-derivatives not containing hydroxyl groups, for example, *m*-dinitrobenzene, evolve a gas when mixed with the magnesium methyl iodide solution, and the volume of gas is considerably increased when the mixture is heated.

It is possible that this evolution of gas is due to the nitro-compound reacting as the tautomeric nitrosophenol or quinone oxime,



but no definite conclusions can be drawn until further experiments have been made.

In each experiment 2—3 hours were allowed to elapse after the flask had been attached to the measuring tube before any readings were taken, due allowance being made for changes of temperature and pressure.

As Tschugaeff informs us that he is conducting further experiments on hydroxy-derivatives, we are not proceeding in this direction, but at present are engaged in applying the method to the determination of amino- and imino-groups.

We are indebted to the Research Fund Committee of the Society for a grant which has helped to defray the expenses incurred in this investigation.

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### XCV.—*Influence of Moist Alcohol and Ethyl Chloride on the Boiling Point of Chloroform.*

By JOHN WADE, D.Sc., and HORACE FINNEMORE, A.I.C.

#### I. *The Existence of a Volatile Impurity in Chloroform made from Alcohol.*

It is usually assumed that commercial chloroform made from acetone is identical with that prepared from alcohol, but recent clinical experience indicates that as an anæsthetic it is distinctly inferior to the alcoholic product; the patient often has an undue tendency to cough and hold the breath, and the prolongation of the time of induction thus brought about materially increases the risk of an overdose.

The most obvious explanation of the difference would be the presence of minute quantities of irritating products of decomposition, such as chlorine, carbonyl chloride or hydrochloric acid. But the chloroform sold for anæsthetic purposes contains about 0·5 per cent. of alcohol, with which its sp. gr. 1·492 at 15° corresponds, and in view of the well-known preservative action of this substance, and of the fact that the anæsthetic had been kept in filled "Winchesters" in a cool, dark cellar, such decomposition seemed unlikely. In fact, no decomposition products were present; the first portion of the distillate obtained from a large quantity of chloroform yielded neither hydrochloric acid nor chlorine when shaken with water, nor even when mixed with concentrated sulphuric acid.

A second possibility was the presence of chlorinated derivatives of condensation products of acetone, but there was no indication of such. The chloroform distilled completely at 60—60·8°, after a small fraction had passed over at 55—60°, and left no residue. When a quantity was allowed to evaporate spontaneously, no foreign odour could be detected at any stage. When shaken for a long time with a small volume of concentrated sulphuric acid, the latter was not rendered

turbid or appreciably discoloured, and on distilling the diluted acid nothing but alcohol could be detected in the distillate.

The chloroform thus freed from alcohol, after washing and drying, was rectified through a Young's pear still-head; after the first few drops it passed over entirely at  $61.1-61.2^{\circ}$ ,\* the sp. gr. of the rectified product being 1.5002 at  $15^{\circ}/15^{\circ}$ . The boiling point of pure chloroform is  $61.1^{\circ}$  (Schiff) or  $61.2^{\circ}$  (Thorpe), and its sp. gr. is 1.5009 at  $15^{\circ}/15^{\circ}$  (Perkin).

Other samples gave the same result. Chloroform, prepared from rectified spirit and methylated spirit, with which no abnormal anæsthetic action had been observed, also behaved in the same way. Commercial chloroform, according to ordinary criteria, appears to be an identical product, whether made from acetone or from alcohol, and to contain no foreign substance other than the alcohol added for preservative purposes.

Nevertheless, clinical experience could not be ignored, and more delicate methods had to be sought in order to ascertain the cause of the undoubted therapeutical difference between the two varieties. The problem was eventually solved with the aid of a Young's evaporator still-head (Trans., 1899, 75, 694).

On systematically fractionating the various specimens through one of these still-heads, having 2 bulbs and 5 sections, a distinct differentiation was obtained. All the specimens gave appreciable fractions (3 to 4 per cent.) below  $60^{\circ}$ ; but whilst the "acetone" chloroform invariably commenced to boil at  $55^{\circ}$ , the chloroform made from alcohol, whether rectified or methylated, began to boil at  $54^{\circ}$ . This difference was fairly constant in all the specimens examined.

The relatively large amount of the fraction  $55-60^{\circ}$  rendered it unlikely that it consisted of a foreign substance, and pointed to a physical cause. Traub (*Wochensh. Chem. Pharm.*, 1892, 11) obtained a similar fraction, which from its sp. gr. 1.185, he concluded to be a mixture of ethylidene chloride and chloroform. The sp. gr. of the present fractions was about 1.45, and they contained appreciable quantities of alcohol; it seemed probable, therefore, that they were mixtures of constant boiling point similar to those which Young (Trans., 1902, 81, 714) has isolated from other alcoholic mixtures.

The boiling point curve of chloroform and alcohol constructed by Thayer (*Amer. Chem. J.*, 1899, 3, 36) from statical observations, indicates the existence of a binary mixture of minimum boiling point at about  $58.5^{\circ}/735.2$  mm. On twice slowly distilling a quantity of the "acetone" chloroform through the evaporator column, a constituent boiling at about  $59.4^{\circ}$  was clearly indicated. The minimum reading from Thayer's statical curve, reduced to 760 mm., is  $59.5^{\circ}$ .

\* All boiling points are corrected and reduced to 760 mm.

*Fractionation of Anæsthetic Chloroform made from Acetone.*

Chloroform, 373 grams. Alcohol, about 0.5 per cent.

B. p. reduced to 760 mm.	Weight.	$\Delta$ .*	B. p. reduced to 760 mm.	Weight.	$\Delta$ .
55.5—57.2	1.5	0.9	60.4—60.6	31.0	155
57.2—58.7	2.9	1.9	60.6—60.8	34.2	171
58.7—59.35	2.4	3.7	60.8—61.0	45.9	229
58.35—59.5	2.0	13	61.0—61.1	111.0	1110
59.5—60.2	3.5	5.0	61.1—61.2	108.0	1080
60.2—60.4	12.5	62	Residue .....	8.8	—
			Loss .....	9.3	—

$$* \Delta = \frac{\text{weight of fraction}}{\text{increment of temperature}}.$$

The quantity was too small to allow of closer investigation, for although on refractionating the earlier fractions the relative amount of the fraction boiling at 59.4° was increased, the absolute amount remained unaltered owing to the unavoidable loss of material. In order to obtain larger quantities, and determine accurately the composition and character of the binary mixture, mixtures containing various proportions of chloroform and alcohol were subjected to the same treatment.

*II. Isolation of a Binary Mixture of Chloroform and Alcohol.*

The chloroform, when purified by the foregoing method and rectified through the evaporator still-head, boiled almost entirely between 61.1° and 61.2°, the greater part passing over at 61.15—61.17°; the sp. gr. was 1.5006 at 15°/15°.

The alcohol, when prepared from commercial absolute alcohol by drying with lime and anhydrous copper sulphate, on rectification through the evaporator still-head boiled entirely at 78.15—78.20°; the sp. gr. was 0.7963 at 15°/15°, corresponding with 0.7 per cent. of water. Thayer's boiling points, which were determined in a modified Beckmann apparatus, are obviously too high; chloroform = 60.93°/744.2 mm., and 60.50°/732.5 mm. = 61.60 and 61.64°/760 mm.; alcohol = 77.86°/744.2 mm. = 78.53°/760 mm.

a. *Chloroform with a Molecular Proportion of Alcohol.*

Chloroform, 80 grams. Alcohol, 31 grams (containing 0.3 gram of water).

B. p. reduced to 760 mm.	Weight.	Δ.	B. p. reduced to 760 mm.	Weight.	Δ.
55.1—56.1	3.8	3.8	65—70	0.6	0.1
56.1—58.6	4.7	1.9	70—75	0.2	0.04
58.6—59.2	11.9	19.8	75—78	1.3	0.4
59.20—59.29	11.0	122	78.20—78.25	2.6	52
59.29—59.32	45.9	1530	78.25—78.30	15.5	310
59.32—60.1	1.9	2.4	Residue .....	5.3	—
60.1—65	2.0	0.4	Loss .....	4.3	—

The first two fractions, 55.1—58.6°, were turbid, and deposited water, which, as will be seen, forms a ternary mixture with the chloroform and alcohol boiling at 55.5°. The bulk of the mixture separated sharply into alcohol and the binary mixture of minimum boiling point. The latter boiled at 59.29—59.32°, and had a sp. gr. 1.4103 at 15°/15°. The alcohol boiled at 78.25—78.30° and had a sp. gr. 0.7963 at 15°/15°; judging from Young's experience in fractionating mixtures of alcohol, benzene, and water (*loc. cit.*), the alcohol was nearly anhydrous; its somewhat high sp. gr. (anhydrous alcohol has a sp. gr. 0.7943 at 15°/15°) therefore indicated the presence of chloroform, which was verified by conversion into phenyl isocyanide.

b. *Chloroform with a slight excess of Alcohol.*

Chloroform, 97.5 grams. Alcohol, 9.0 grams (containing 0.06 gram of water).

B. p. reduced to 760 mm.	Weight.	Δ.	B. p. reduced to 760 mm.	Weight.	Δ.
55.2—58.2	3.2	1.1	59.25—59.30	6.3	126
58.2—59.15	8.5	9.0	59.30—59.40	71.1	711
59.15—59.25	6.9	69	Residue .....	6.9	—
			Loss .....	3.6	—

The first fraction was turbid and deposited water, with which the slight excess of alcohol had been carried over. On separating the water and redistilling the first four fractions, a further quantity of

11.2 grams of the binary mixture was obtained. The latter boiled at 59.30—59.40°, and had a sp. gr. 1.4095 at 15°/15°.

*c. Alcohol with Excess of Chloroform.*

Chloroform, 139 grams. Alcohol, 5.7 grams (containing 0.04 gram of water).

B. p. reduced to 760 mm.	Weight.	Δ.	B. p. reduced to 760 mm.	Weight.	Δ.
55.1—58.85	5.4	1.3	59.85—60.35	4.7	9.4
58.85—59.25	8.1	20.2	60.35—60.85	9.4	18.8
59.25—59.34	6.6	73	60.85—61.05	6.4	32
59.34—59.37	6.0	200	61.05—61.15	6.4	64
59.37—59.39	43.4	2170	61.15—61.25	23.5	235
59.39—59.45	10.4	173	Residue .....	6.4	—
59.45—59.85	3.6	9.0	Loss .....	4.4	—

The first fractions were turbid and deposited water. About half the mixture separated sharply into the binary mixture and chloroform. The binary mixture boiled at 59.37—59.39°, and had a sp. gr. 1.4112 at 15°/15°. The chloroform boiled at 61.15—61.25°, and had a sp. gr. 1.5000 at 15°/15°; it evidently contained a trace of alcohol, the presence of which was verified by shaking with a little concentrated sulphuric acid and distilling the diluted extract; the distillate yielded recognisable quantities of iodoform and acetaldehyde.

The three binary products were thus practically identical :

Original mixture	B. p. of binary mixture reduced to 760 mm.	Sp. gr. at 15°/15°
Large excess of alcohol .....	59.29—59.32°	1.4103
Slight „ „ .....	59.30—59.40	1.4095
Large excess of chloroform...	59.37—59.39	1.4112

On redistilling the united products the sp. gr. and reduced boiling point were found to vary slightly with the barometric pressure, confirming their physical character.

Barometer.	B. p. reduced to 760 mm.	Sp. gr. at 15°/15°.	Percentage of alcohol.
769.9	59.35°	1.4112	7.06
764.0	59.40	1.4120	7.01

The minimum point of Thayer's statical curve corresponds with about 7 per cent. of alcohol. In calculating the composition of the above products from the sp. gr., allowance was made for the slight contraction which occurs on mixing chloroform and alcohol. A mixture of 61.924 grams of chloroform (sp. gr. 1.5002 at 15°/15°) and 4.629 grams of alcohol (sp. gr. 0.7963 at 15°/15°), containing 6.95 per cent. of alcohol, had a sp. gr. 1.41255 at 15°/15°. The percentage of alcohol calculated from this, assuming no change of volume, is 6.61, from which it follows that there is a contraction of 0.31 per cent.

The distillation of a fraction of ordinary anæsthetic chloroform between 59.35° and 61.15° is thus explained. The formation of the fraction 55—59.35° now remained to be elucidated. This fraction invariably contained water, which separated at once from the distillate, and from analogy with Young's work on mixtures of benzene alcohol, and water (*ibid.*, 739) the formation of a ternary mixture more volatile than either of the possible binary mixtures was probable. This proved to be the case. A binary mixture of chloroform and water was also isolated.

### III. *Isolation of a Binary Mixture of Chloroform and Water.* a. *Chloroform in Excess.*

Chloroform, 180 grams. Water, 1.5 grams.

The water floated as a large bubble on the chloroform.

B. p. reduced to 760 mm.	Weight.	Δ.	B. p. reduced to 760 mm.	Weight.	Δ.
56.0—56.2°	54.7	273	59.6—60.0°	20.0	50
56.2—56.6	17.9	45	60.0—60.5	25.2	50
56.6—58.4	10.5	5.8	60.5—61.0	28.0	56
58.4—59.6	11.2	9.3	Residue .....	4.4	—
			Loss .....	9.6	—

The temperature at once rose to 56°, and the binary mixture distilled at 56—56.2°; it was clear, but about 2.5 per cent. of water had separated on condensing; the sp. gr. of the filtered distillate was 1.4993 at 15°/15°. After drying over calcium chloride and redistilling the sp. gr. was 1.5005 at 15°/15°. The chloroform which followed the binary mixture was not dry, and water was still visible in the residue and distillate.

b. *Water in Excess.*

Chloroform, 120 grams. Water, 40 grams.

The chloroform was turbid, but became clear on warming; the supernatant water was clear.

B. p. reduced to 760 mm.	Weight.	Δ.	B. p. reduced to 760 mm.	Weight.	Δ.
56.0—56.1°	18.1	181	56.4—99.7°	3.7	0.09
56.1—56.2	85.4	854	99.7—100.0	30.8	103
56.2—56.4	10.8	54	Residue .....	6.0	—
			Loss .....	5.2	—

The binary mixture distilled at 56.1—56.2°, and was clear, about 2.5 per cent. by weight of water having separated on condensing. The sp. gr. of the filtered distillate was 1.4986 at 15°/15°, and after drying and redistilling was 1.5003 at 15°/15°. The water which followed the binary mixture was nearly free from chloroform; it boiled at 99.9—100° and had a sp. gr. 1.002 at 15°/15°.

IV. *Isolation of a Ternary Mixture of Chloroform, Alcohol and Water.*  
a. *Alcohol in Excess.*

Chloroform, 120 grams. Alcohol, (99.3 per cent.) 46 grams. Water, 9 grams.

The mixture of chloroform and alcohol was saturated with water, and was just clear at 15°.

B. p. reduced to 760 mm.	Weight.	Δ.	B. p. reduced to 760 mm.	Weight.	Δ.
55.15—55.4°	2.5	10	77.5—78.15°	5.2	8.0
55.4—55.5	115.8	1158	78.15—78.25	7.3	73
55.5—58.0	6.4	2.6	78.25—78.30	26.7	534
58—74	1.7	0.1	Residue .....	4.0	—
74—77.5	2.8	0.8	Loss .....	2.6	—

The ternary mixture distilled at 55.4—55.5°, and was turbid, about 3.5 per cent. by weight of water immediately separating. The sp. gr. of the filtered liquid was 1.4498 at 15°/15°. After drying with lime and redistilling the whole, the sp. gr. was 1.4500 at 15°/15°; the

amount of dissolved water in the original distillate was therefore very small. The alcohol boiling at  $78.25-78.30^{\circ}$  had a sp. gr. 0.8183 at  $15^{\circ}/15^{\circ}$ , corresponding with 8.2 per cent. of water; according to Noyes and Warfel (*J. Amer. Chem. Soc.*, 1901, 23, 467) alcohol containing 8 to 9 per cent. of water boils at  $78.26-78.27^{\circ}$ . A trace of chloroform was present, which was identified as before by conversion into phenyl isocyanide. Water being in excess throughout, the binary mixture of chloroform and alcohol could not be formed.

b. *Chloroform in Slight Excess.*

Chloroform, 120 grams. Alcohol, (99.3 per cent.) 4.6 grams. Water, 2.0 grams.

The mixture was turbid, and cleared on boiling, but the water did not entirely dissolve.

B. p. reduced to 760 mm.	Weight.	$\Delta$ .	B. p. reduced to 760 mm.	Weight.	$\Delta$ .
55 — 55.45°	2.7	6	58.35—58.65°	5.2	17
<b>55.45—55.55</b>	<b>26.2</b>	<b>262</b>	58.65—58.95	5.3	18
55.55—55.85	9.4	31	58.95—59.25	5.9	20
55.85—56.05	7.2	36	<b>59.25—59.45</b>	4.4	<b>22</b>
56.05—56.35	4.9	16	59.45—59.75	5.5	18
56.35—57.15	4.3	5.4	59.75—60.15	5.9	15
57.15—58.05	8.1	9	60.15—60.65	16.8	34
58.05—58.35	4.5	15	Residue .....	5.9	—
			Loss .....	4.4	—

The ternary mixture distilled at  $55.45-55.55^{\circ}$ , and was turbid, about 3.5 per cent. of water immediately separating. The sp. gr. of the filtered liquid was 1.4502 at  $15^{\circ}/15^{\circ}$ . The presence of the binary mixture of chloroform and alcohol is clearly indicated in the fraction  $59.25-59.45^{\circ}$ .

A mixture of chloroform and alcohol of sp. gr. 1.4500 at  $15^{\circ}/15^{\circ}$  contains 4.1 per cent. of alcohol. Taking the water in the original distillate at 3.5 per cent. (the estimation is only approximate), the percentage composition of the ternary mixture is :

Chloroform .....	92.5
Alcohol .....	4.0
Water .....	3.5
	<hr/>
	100.0

V. *Identification of Anæsthetic Chloroform made from Acetone.*

The possible constituents of constant boiling point which may be isolated from a mixture of chloroform, alcohol, and water are therefore :

Constituent.	B. p.	Composition.		
		Chloroform.	Alcohol.	Water.
1. Ternary C.A.W. ....	55·5°	92·5	4·0	3·5
2. Binary C.W. ....	56·1	97·5	—	2·5
3. „ C.A. ....	59·4	93·0	7·0	—
4. Chloroform C. ....	61·15	100	—	—
5. Binary A.W. (Young)...	78·15	—	95·5	4·5
6. Alcohol A. ....	78·3	—	100	—
7. Water W. ....	100	—	—	100

It follows that pure chloroform containing some alcohol and a trace of water will behave on distillation precisely as the anæsthetic chloroform made from acetone. The temperature will rise at once to about 55·5, when the water will pass over with a part of the alcohol and some chloroform as a ternary mixture. The remainder of the alcohol will then pass over with chloroform as a binary mixture at 59·4. Finally pure chloroform will be left, boiling at 61·15°. The anæsthetic chloroform made from acetone is therefore a pure product, and contains no foreign substance other than the preservative alcohol and a trace of water.

VI. *Identification of Ethyl Chloride in Chloroform made from Alcohol.*

The nature of the fraction 54—55° obtained from the chloroform prepared from alcohol remained to be determined. The foreign substance which the above results show to be present must be a liquid considerably more volatile than chloroform. Since the pure chloroform made from acetone has proved in practice to be somewhat slow and irregular as an anæsthetic, the foreign liquid, as it removes the irregularity and diminishes the time of induction, must have anæsthetic properties more rapid than those of pure chloroform. Further, this foreign volatile anæsthetic must be such as can be formed

from alcohol in the course of chlorination, but cannot be formed from acetone. It cannot arise from the action of decomposition products of chloroform on the preservative alcohol, or it would be equally present in the chloroform made from acetone.

Ethyl chloride obviously meets these requirements; it is very volatile and is extensively used instead of nitrous oxide as a rapid temporary anæsthetic; complete anæsthesia is induced by three or four inhalations of the vapour, whereas chloroform requires as many minutes. Finally it may be easily formed from alcohol in the course of chlorination, just as in the manufacture of chloral, whilst it is difficult to see how it could be formed from acetone under these conditions.

On the other hand it seemed improbable that a liquid boiling at  $12^{\circ}$  should distil even in small proportion with a much less volatile mixture at  $54-55^{\circ}$ . Experiment showed, however, that the addition of 0.2 and 0.1 per cent. of ethyl chloride to pure chloroform containing alcohol gave products which behaved on distillation like the chloroform prepared from alcohol, although in an exaggerated manner.

*a. Chloroform with Alcohol and 0.2 per cent. of Ethyl Chloride.*

Chloroform 300 grams. Alcohol 1.5 grams. Ethyl chloride 0.6 grams.

B. p. reduced to 760 mm.	Weight.	$\Delta$ .	B. p. reduced to 760 mm.	Weight.	$\Delta$ .
51 —55°	0.8	0.2	59.1—59.7°	1.8	3.0
55 —57	0.7	0.35	59.7—59.9	1.4	7.0
57 —57.9	0.6	0.7	59.9—60.1	2.8	14
57.9—59.1	1.4	1.2	60.1—60.3	5.8	29

The boiling point is thus lowered about  $4^{\circ}$  by 0.2 per cent. of ethyl chloride, and the indications of the binary mixture of chloroform and alcohol are at the same time obliterated.

b. *Chloroform with Alcohol and 0.1 per cent. of Ethyl Chloride.*

Chloroform 300 grams. Alcohol 1.5 grams. Ethyl chloride 0.3 grams.

B. p. reduced to 760 mm.	Weight.	$\Delta$ .	B. p. reduced to 760 mm.	Weight.	$\Delta$ .
52.65—54.85°	0.25	0.1	58.75—59.25°	0.95	1.9
54.85—56.85	0.45	0.2	<b>59.25—59.45</b>	0.95	<b>4.7</b>
56.85—57.85	0.50	0.5	59.45—59.65	0.50	2.5
57.85—58.15	0.50	1.7	59.65—59.85	1.25	6.2
58.15—58.75	0.70	1.2	59.85—59.95	2.79	27.9

The boiling point is therefore lowered about 2° by 0.1 per cent. of ethyl chloride, and there is a clear indication of the binary mixture of chloroform and alcohol at 59.25—59.45°.

The presence of a minute quantity of ethyl chloride in chloroform made from alcohol, probably about 0.05 per cent.\* would thus account for its physical behaviour. A direct chemical proof was nevertheless desirable. It was obviously impossible to isolate the ethyl chloride as such on a laboratory scale, and the only possibility of chemical proof was to convert it into some more readily isolated and better characterised derivative, the substance eventually selected being propionic acid. Preliminary experiments proved that the above volatile fractions, undoubtedly containing ethyl chloride, yield recognisable amounts of silver propionate when treated in the manner described below, whilst the most volatile fractions from pure chloroform containing alcohol yielded neither propionate, nor any substance which could be mistaken for it.

Specimens of chloroform made from rectified and methylated spirit and from acetone were fractionated as before, the distillates being collected in a freezing mixture. The first small fraction of each was heated with potassium cyanide and 80 per cent. alcohol in a sealed tube for several hours at 100°, and finally for 1 hour at 120°. The contents of the tubes separated from potassium chloride and humous matter were distilled to dryness on a water-bath. The distillates, which contained ethyl formate due to the hydrolysis of the chloroform, as well as hydrogen cyanide and possibly propionitrile, were heated in a reflux apparatus until ammonia ceased to be evolved. After removing the alcohol, the acids were liberated with dilute sulphuric acid, and converted into silver salts by prolonged boiling with silver

\* About 2 c.c. per Winchester quart.

oxide, in the course of which most of the silver formate was destroyed. The aqueous solution was then evaporated to dryness at  $100^{\circ}$  to destroy the last traces of formate. All the specimens were subjected as nearly as possible to identical treatment.

The chloroform made from acetone gave no soluble residue, and no coloration was obtained on adding a drop of ferric chloride solution to the blackened residue which was left after the destruction of the last traces of silver formate. There was no silver propionate present, and no ethyl chloride in the original chloroform.

The chloroform prepared from alcohol left in both cases a few milligrams of soluble residue, which was identified as silver propionate. Portions ignited gave vapours having the odour of acetic or propionic acid, and not that of butyric or higher acids. The salt then fused in a characteristic manner, leaving a smooth residue of silver; silver propionate and its higher homologues do this, but silver acetate only sinters when ignited, the metal retaining the granulated form of the salt. The silver salts gave a red coloration with ferric chloride, which was precipitated in a characteristic manner on boiling, and destroyed by a drop of dilute hydrochloric acid. The fact that the residues from pure chloroform and the chloroform prepared from acetone gave no coloration with ferric chloride was sufficient evidence of the elimination of formic acid. The silver salt obtained from chloroform to which a small quantity of ethyl chloride had been added behaved throughout in a precisely similar manner.

The volatile substance which improves the anæsthetic properties of chloroform made from alcohol, but is absent from chloroform made from acetone, is therefore ethyl chloride. This conclusion has been substantiated by direct clinical experience, for an account of which, as of the observations previously quoted, we are indebted to Mr. G. Rowell, F.R.C.S., Senior Anæsthetist to Guy's Hospital. "Acetone" chloroform to which a small quantity of ethyl chloride has been added is therapeutically identical with chloroform made from alcohol, and it is probable that the addition of a further quantity of ethyl chloride will be even more beneficial in decreasing the time of induction and generally facilitating anæsthesia. The loss even with 1 per cent. of ethyl chloride is trifling at ordinary temperatures, but above this proportion the mixture is not permanent.

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# XCVI.—*The Mechanical Analysis of Soils and the Composition of the Fractions Resulting Therefrom.*

By ALFRED DANIEL HALL, M.A.

## *Introduction.*

THE mechanical analysis of soils, by which is meant the sorting out of the particles of the soil into groups, each of which contains material lying between specified limits of size, has long occupied the attention of agricultural chemists, although in this country, as compared with Germany or the United States, it has been but little practised. The importance of this determination lies in the fact that the behaviour of the soil towards water, its power of retaining and handing over the rainfall to the plant, and also its physical texture and amenability to cultivation—factors which are of greater importance in the nutrition of the crop than the amount of plant food present—are determined by the sizes of the particles of which the soil is composed. Without referring in detail to the voluminous literature which has grown up round the subject it will be sufficient here to quote one or two of the more important papers illustrating the principles on which the process is based. The various methods in use may be divided into two groups; in one, the separation is effected by a stream of running water, the velocity of which is increased to carry over successively coarser particles, in the other by leaving the turbid mixture of soil and water to settle for given periods of time, the longer the time interval the finer being the group of particles remaining suspended. The former method was made quantitative by Schöne (*Über Schlamm-analyse*, Berlin, 1867), and as modified by A. Meyer (Wollny's *Forsch. der Agricultur. physik.*, 1882, 5, 228) is in general use in Germany (Wahnschaffe, *Anleitung zu Wissenschaftlichen Bodenuntersuchung*, Berlin, 1903). The apparatus has been still further improved and the whole method reduced to an accurate form by Hilgard (*Amer. J. Sci.*, 1873, 6, 288; U.S.A. Division of Chemistry, 1893, *Bulletin* 38, p. 60) to whom we are indebted for a considerable elucidation of the whole subject. The second method, depending on sedimentation for a given time, was elaborated by Wolff (*Untersuchung. landw. Stoffe*, Berlin, 1875) and critically discussed by Osborne (*Conn. Agric. Exp. Station Report*, 1886, p. 141; 1887, p. 144) who showed that it would yield the same result as the running water method of Hilgard. With sundry modifications in detail, Osborne's method is now employed by the United States Division of Soils in the extensive soil survey which that Department is executing (U.S.A. Dept. of Agriculture,

Division of Soils, 1896, *Bulletin* 4). In all the foregoing methods the soil is freed from its coarser particles by a system of sieves, and then the loose aggregates of the finer particles are, as far as possible, broken up either by long continued boiling with water or by rubbing the paste of soil and water with a soft pestle formed from an india-rubber bung.

A fundamental modification of the whole process was introduced by Schlœsing (*Compt. rend.*, 1874, 78, p. 1276), who began by a preliminary treatment of the soil with dilute acid, then removed the salts and excess of acid by washing, and finally added a little ammonia to the liquid in which the soil was afterwards suspended. Schlœsing himself employed a simple sedimentation process which divided the residue into two fractions only, but it is clear that any method of fractionating the soil residue may be used, the essential difference being that in one case the soil is first washed with acid, whereas in the other the process is carried out on the raw soil. Schlœsing's method has not been widely adopted out of France; Petermann however followed it in his examination of Belgian soils (*Recherches de Chimie*, Brussels, 1898), and it is also employed officially in Italy (*Staz. Sperimentale Agrarie Italiane*, 1891, 17, 672).

The object of the preliminary treatment with acid is twofold, in the first place calcium carbonate is removed, secondly the "humates" which are present in surface soils are decomposed and the liberated humic acid becomes soluble in the ammoniacal liquid in which the sedimentation is afterwards conducted. In soils containing any large proportion of organic matter, such as the pastures and many of the arable soils of this country, the amount of the humates is sufficient to bind together a considerable quantity of the finest particles into loose aggregates which resist disintegration by the boiling or pestling preliminary to working on the raw soil. In other soils, calcium carbonate serves the same purpose of a temporary cement for the finest particles, even the weathering and management of the soil has the same effect of causing the material of a clayey nature to flocculate into loose aggregates, which behave as larger agglomerations. Again the power possessed by soluble salts of inducing flocculation of the clay particles is well known (compare Joly, *Mécanisme intime de la Sedimentation*, VIII Congress Géologique International, 1900); hence Schlœsing's method presents an advantage in that it removes all soluble salts and conducts the sedimentation in a practically uniform medium containing free ammonia in order to induce a maximum of deflocculation. How potent the presence of salts may be in causing flocculation may be seen from the following experiments, in which two pure clays were separated into fractions by

sedimentation in pure water and in solutions containing 0.04 per cent. of sodium chloride and calcium sulphate respectively.

250 c.c. water with	10 grams china clay.			10 grams modelling clay.		
	0.	Salt (0.1 gram).	Gypsum (0.1 gram).	0.	Salt (0.1 gram).	Gypsum (0.1 gram).
Falling in 1 minute .....	2.22	2.54	2.28	0.53	0.45	0.41
Suspended for 1, but fall- ing in 25 minutes .....	3.91	6.04	7.30	1.45	8.76	8.30
Suspended for 25 minutes, but falling in 24 hours...	2.08	1.50	0.37	2.33	0.9	1.38
Suspended for 24 hours ...	2.00	—	—	5.53	—	—
Total.....	10.21	10.08	9.95	9.84	10.11	10.09

Speaking generally, it is found that the preliminary treatment with acid gives a greater proportion of the finest order of particles (clay) than is obtained by working on the raw soil. Yet the acid employed is too weak to dissolve any appreciable amount of mineral material other than calcium carbonate, and the attack must be mainly directed towards those very fine particles which are so small as to approach the condition of dissolved matter. As then the acid treatment cannot create clay particles, its action would seem to consist in completing the work of resolving the temporary aggregates which is largely but not wholly brought about by the boiling or pestling processes in the other method; it, therefore, must give a more accurate measure of the proportion of these finest particles present in the original soil. For these reasons it seemed desirable to submit the two processes to a critical comparison, for Osborne (*loc. cit.*), who tried both Schläesing's method and his own on the same soils, did not attempt to divide the soil after washing with acid into the same series of fractions as he obtained from the raw soil, but followed Schläesing's division into a clay fraction and a single sand fraction, with the result that the two sets of results are not comparable. In order to secure a critical examination of the methods it was necessary to work on soils which are identical as regards their original physical structure, but which by processes of cultivation have assumed very different textures, so that in some there may be little and in others much of the finest material bound into the temporary aggregates which it is the function of the acid to resolve. For this purpose the Rothamsted soils provide examples of exceptional value; the management of each of the

Rothamsted plots has been unchanged for 50 or even 60 years, some of them have been receiving organic manures annually during the whole period, others have been entirely unmanured or have been receiving only mineral salts, and are, therefore, much depleted of their original store of organic matter. As a natural consequence, the physical texture, as shown by the tilth, by their tendency to dry into a stony or a friable condition, by the ease with which they can be cultivated, and by their water-retaining power, varies considerably in passing from plot to plot, yet it cannot be considered that the fundamental physical constitution of the soils has been sensibly altered, so small a fraction of the whole weight even of the surface soil is the sum of all the manures added during the experimental period.

It is assumed that the preferable method of mechanical analysis is that showing the essential identity of soils from neighbouring plots which may have acquired very dissimilar textures through differences of cultivation, since information is thus obtained as to the permanent rather than the temporary characteristics of the soil. It has been argued that the problem is not to ascertain the fundamental constitution but the current condition of the soil; that if, as is assumed, the working nature of the soil depends on the size of the particles, it matters little whether they are solid as with a sandy soil, or aggregates of smaller particles behaving like larger units as with a clay soil in a good state of tilth. But in the one case, unskilful management will ruin the tilth, which in the other is practically independent of the treatment, and although the two soils may for the time be similar the analysis should aim at gauging their capacity and behaviour under all conditions by determining their real nature. If once the mechanical analysis provides an accurate description of the mineral framework of the soil, a consideration of other factors, such as the proportion of humus and calcium carbonate, may enable the analyst to form an idea of their actual texture. But no method of mechanical analysis can actually measure the texture, a problem which if it is soluble at all in the laboratory must be attacked by other processes.

### *The Soils Examined.*

The soils selected for analysis have been derived from the Rothamsted experimental fields; these fields are scattered about the estate and differ somewhat in texture, so that the results for a given field are only comparable among themselves. The soil is a strong flinty loam derived from the "clay with flints" which covers much of the chalk plateau in Hertfordshire; the subsoil is distinctly irregular, a neighbouring exposure showing besides the true "clay with flints" pockets of almost unaltered "plastic clay" and of "tertiary" sand. The fields,

with the exception of Barn Field, are nearly level, and there is evidence that the experimental portions were sensibly uniform at the start.

The *Broadbalk Field* has grown wheat every year since 1844. Of the soil samples examined Nos. 1, 2, 3, 4, were drawn in 1893, and Nos. 25, 26, 27, in 1904.

No. 1. Plot 2, received 14 tons of farmyard manure every year (50 years).

No. 2. Plot 3, unmanured every year (50 years).

No. 3. Plot 6, received  $3\frac{1}{2}$  cwt. of superphosphate, 200 lbs. of potassium sulphate, 100 lbs. each of sodium and magnesium sulphates, 100 lbs. each of ammonium sulphate and chloride every year since 1852 (42 years).

No. 4. Plot 9, received a similar manuring to Plot 6, except that the ammonium salts were replaced by an average of 500 lbs. of sodium nitrate added annually over the 42 years.

No. 25. Plot 3, unmanured (61 years).

No. 26. Plot 6, manured as described above (53 years).

No. 27. Plot 9, manured as described above (53 years).

The *Hoos Field* has grown barley every year since 1852. The samples for analysis were drawn in 1903.

No. 5. Plot 10, unmanured every year (52 years).

No. 6. Plot 2A, received  $3\frac{1}{2}$  cwt. of superphosphate, 100 lbs. each of ammonium sulphate and chloride every year.

No. 7. Plot 2AA, received  $3\frac{1}{2}$  cwt. of superphosphate and 275 lbs. of sodium nitrate.

*Hoos Potato Land* is a part of the same field which grew potatoes for 26 years, 1876—1901, after which it has grown barley without further manuring. Samples were drawn in 1903.

No. 8. Plot 1, unmanured continuously.

No. 9. Plot 3, received 14 tons per acre of farmyard manure every year (26 years).

No. 10. Plot 5, received 200 lbs. each of ammonium sulphate and chloride.

No. 11. Plot 6, received 550 lbs. of sodium nitrate.

The *Park* is grass-land mown for hay each year and has received the same manures since 1856 (48 years). The samples were drawn in 1904.

No. 12. Plot 3, unmanured continuously.

No. 13. Plot 9, received  $3\frac{1}{2}$  cwt. of superphosphate, 500 lbs. of potassium sulphate, 100 lbs. each of sodium and magnesium sulphates, 200 lbs. each of ammonium sulphate and chloride.

No. 14. Plot 14, received the same treatment as Plot 9 except that the ammonium salts were replaced by 550 lbs. of sodium nitrate.

The *Barn Field* has been under cultivation for roots since 1843, and

for the last 28 years has grown mangels, the manurial treatment has been practically continuous for each plot since 1856 (48 years). Soil samples were drawn in 1903.

No. 15. Plot 1o, received 14 tons per acre of farmyard manure every year.

No. 16. Plot 4o, received  $3\frac{1}{2}$  cwt. of superphosphate, 500 lbs. of potassium sulphate, 200 lbs. of sodium chloride, 200 lbs. of magnesium sulphate.

No. 17. Plot 1c, received 14 tons of farmyard manure, and 2000 lbs. of rape cake every year.

No. 18. Plot 4c, received the same treatment as 4o, with the addition of 2000 lbs. of rape cake annually.

No. 19. Plot 4A, received a similar treatment to 4c, except that the rape cake was replaced by 200 lbs. each of ammonium sulphate and chloride.

No. 20. Plot 4N, received a similar treatment to 4A and 4c, except that the nitrogenous manure was 550 lbs. of sodium nitrate instead of the ammonium salts or rape cake.

No. 21. Plot 5A, received  $3\frac{1}{2}$  cwt. of superphosphate, and 200 lbs. each of ammonium sulphate and chloride.

No. 22. Plot 5N, received a similar treatment to 5A, except that the ammonium salts were replaced by 550 lbs. of sodium nitrate.

The *Barnfield Grass-land* was originally part of the preceding field, but was laid down to grass in 1874; no record has been kept of its occasional manurings.

No. 23. Sample drawn from the portion next to Plot 1o.

No. 24. Sample drawn from the portion next to Plot 1c.

All the samples are taken to a depth of nine inches unless otherwise stated.

In all cases the soil sample is dried at a temperature not exceeding  $40^{\circ}$ , roughly powdered, and passed through a sieve with round holes 3 mm. in diameter, and all the analyses were made on the air-dried fine earth passing this sieve.

### *Method of Analysis.*

Ten grams of the fine earth are treated with 100 c.c. of  $N/5$  hydrochloric acid, the acid being renewed if it is not sufficient to dissolve all the calcium carbonate present. The soil is rubbed up for some time without the application of pressure with a soft pestle made of an india-rubber bung at the end of a glass rod; this pestling may be conveniently effected by the aid of a small water turbine. The undissolved material is then thoroughly washed until free from acid and may be collected on a filter, dried and weighed to ascertain the loss

on solution, or washed immediately into the sedimenting vessel. In either case after being freed from acid it is thoroughly pestled again with water to which a few c.c. of strong ammonia have been added. A lipped beaker (about 10 cm. high, and 7 cm. in diameter) is employed with marks at 8.5 and 7.5 cm. from the bottom; into this the mixture of soil and water is washed through two sieves, the first having round holes 1 mm. in diameter, the second being a woven wire sieve No. 100 brass wire cloth, 100 meshes to the inch. The material arrested by the sieves is dried, weighed, ignited and reweighed. The beaker is filled to the mark with water and left undisturbed for 24 hours. The turbid liquid is then decanted from the sediment, which is rubbed up afresh with a few c.c. of ammonia, water is added to the mark, and the 24 hours' sedimentation is repeated. The whole process is repeated day by day until the supernatant liquid is clear after 24 hours; that is, until all the particles which will not fall 8.5 cm. in 24 hours are removed. Generally about eight decantations are sufficient, but with some soils as many as fifteen may be required. The turbid liquid poured off is evaporated, and the residue dried in the steam oven, weighed, ignited over an argand burner and weighed again, or the turbid liquid may be coagulated by acidifying and the residue collected by decantation. The sediment remaining in the beaker is worked up afresh in the same way, the water being only added to a depth of 7.5 cm., and left for 2 hours 5 minutes; the process is repeated as before until all the material remaining suspended for that period is removed. The decanted liquid is again evaporated, the residue is dried in the steam oven, weighed, ignited and reweighed. A third decantation follows with a water column 7.5 cm. in height, and the time of settlement 12.5 minutes; lastly comes a decantation for 75 seconds with a height of 7.5 cm. as before. Thus the whole of the fine earth is divided into seven fractions, the two coarsest by means of sieves, the five finest by settlement from water.

The times of settlement and the height of the water column are purely arbitrary and may be varied at will in order to secure fractions of any desired diameter, the size obtained being determined by actual measurement under the microscope.

The whole process is a tedious one, requiring something like three weeks for its completion and the evaporation of 20 litres or more of water. It can be shortened by the introduction of centrifugal methods whereby the force of gravity causing the fall of the particles is replaced by a much stronger centrifugal force (U.S.A. Department of Agriculture, *Yearbook*, 1900, p. 399; Kilroe, *Proc. Roy. Dublin Soc.* 1904, I. [v], 223). Otherwise it admits of no acceleration. But with systematic working a number of determinations can be carried on simultaneously, and except in the first and final stages, these demand but little time from day to day.

The following table gives the approximate size of the particles in each of the fractions obtained by the foregoing method. Examination under the microscope showed that whilst no fraction was absolutely free from smaller particles the bulk fell within the specified limits.

TABLE I.

Sizes of particles in the groups separated by mechanical analysis.

	Diameter in mm.	
	Max.	Min.
1st Sieve .....	3.0	1.0
2nd „ .....	1.0	0.2
1st Sediment .....	0.2	0.04
2nd „ .....	0.04	0.01
3rd „ .....	0.01	0.004
4th „ .....	0.004	0.002
“ Klay ” .....	0.002	—

The groups of particles obtained in a mechanical analysis do not possess any definite chemical individuality; in the coarser grained fractions worn grains of quartz predominate, mixed with an increasing proportion of hydrated aluminium silicate and ferric oxide as the size of the particles becomes less, but even the finest fractions contain some free quartz. The following series of determinations show that whilst the coarsest fraction separated by sedimentation contains in the ignited state more than 90 per cent. of quartz and only 7.4 per cent. of aluminium silicate, the finest contains about 10 per cent. of quartz and 67 per cent. of aluminium silicate.

TABLE II.

Partial analyses of soil fractions separated by mechanical analysis involving a preliminary washing with acid.

Samples ignited to remove organic matter before analysis.

Nature of sample.	SiO <sub>2</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	Al <sub>2</sub> O <sub>3</sub> .
1st Sediment * ...	94.6	1.1	3.4
2nd „	92.0	1.2	6.2
3rd „	88.3	1.8	8.5
4th „	61.7	7.0	23.4

\* Mixed samples.

TABLE II (*continued*).

Nature of sample.		SiO <sub>2</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	Al <sub>2</sub> O <sub>3</sub> .
"Klay"	No. 22	45.6	12.8	30.1
"	" 21	45.4	12.2	30.3
"	" 20	46.3	12.4	33.8
"	" 19	47.3	12.7	31.6
"	" 4	45.2	11.8	29.9
"	" 3	44.7	12.4	30.3
"	" 8	48.6	10.5	31.2
"	" 10	44.5	12.5	29.9
Mean of "Klays"		45.9	12.2	30.9

The presence of organic matter does not permit of an exact determination of the proportion of water of hydration, but by recalculating the analyses (which were all made on samples after ignition) on the assumption that the alumina is combined as  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ , the approximate percentage composition of the finest fraction would be: kaolinite, 72—75; ferric oxide, 11—12; quartz, 9—10; alkalis and alkaline earths, &c., 4—6; nor is there much variation from this mean, at least in dealing with soils of similar origin, as with these from the Rothamsted fields.

It is probable that the physical properties of the soil are dependent on the size rather than on the chemical nature of the constituent particles, being determined in the main by the extent of the surface they expose. Deposits may be found consisting mainly of very finely divided quartz, which have all the properties usually associated with clay soils, the opposite case of coarse-grained kaolinitic material—chemically clay—but behaving more like sand, also occurs. Hence, a difficulty arises in giving the name of "clay" to the finest fraction obtained by mechanical analysis, and it has been suggested that this fraction should be distinguished by the designation "klay," this being defined as the material existing in the soil which possesses a diameter of less than 0.002 mm.

The theory of a particle falling through a viscous liquid has been considered by Stokes (*Trans., Camb. Phil. Soc.*, 1851, 9, 8), who dealt with the motion of small water drops like fog through the air, and by Barus (*Amer. J. Sci.*, 1889, 37, 122). From Stokes's paper is derived the following formula:

$$v = \frac{2ga^2(\sigma - \rho)}{9\eta},$$

for the velocity of the falling particle, where  $\sigma$  is the density of the

particle,  $\alpha$  its radius taken as a sphere,  $\rho$  the density, and  $\eta$  the coefficient of viscosity of the medium. Utilising this formula, the following diameters are obtained for the particles which just fall in the times specified for each group.

Sediment.	Limiting velocity of fall.	Diameter in mm.		
		Calculated at		Minimum by observation.
		10°.	16°.	
1st .....	7.5 cm. in 75 seconds	0.040	0.037	0.01
2nd .....	7.5 „ 750 „	0.0126	0.0116	0.01
3rd .....	7.5 „ 7500 „	0.0040	0.0037	0.004
4th .....	8.5 „ 86400 „	0.00126	0.00126	0.002

The agreement is as close as can be expected considering that the particles are not spherical, and that no precautions are taken to avoid convection currents due to change of temperature during the longer intervals of sedimentation. The use of a dilute solution of ammonia of uncertain strength instead of pure water might be thought to vitiate the value attached to  $\eta$ , the coefficient of viscosity, but a series of comparative measurements shows that various ammonia solutions, up to a much greater strength than is ever attained in carrying out the foregoing method, possess sensibly the same viscosity as pure water through a greater temperature range than that of an ordinary laboratory.

#### *Examination of Soils Rich and Poor in Humus.*

Analyses have been made by the foregoing method of eighteen of the Rothamsted soils, six being rich in humus through the accumulation of organic manures or after lying for some time in pasture, twelve being deficient because of continuous cropping either without manure or with mineral salts only. In order to obtain a critical opinion as to the effect of the preliminary washing in acid, the same eighteen soils have also been analysed without such treatment, that is, the raw soil has been rubbed up in distilled water only and separated by sieves and by sedimentation, using precisely the same times of settlement and distances of falling.

The results are set out in the following tables, of which Table III gives the results when the material is weighed after drying at 100°, and Table IV after ignition to remove organic matter.

TABLE III.—*Mechanical Analyses of Rothamsted Soils.*  
*Percentages after drying at 100°*

Number	1	2	4	25	26	27	8	9	16	15	23	18	17	24	19	21	20	22
	Broadbalk, 1893.			Broadbalk, 1904.			Hos. potato, 1903.			Barnfield mangel and grass soils, 1903.								
	Dung.	Unmanured.	Minerals and nitrate.	Unmanured.	Minerals and ammonium salts.	Minerals and sodium nitrate.	Unmanured.	Dung.	Minerals only.	Dung.	Grass-land.	Minerals and rape-cake.	Dung and rape-cake.	Grass-land.	Minerals and ammonium salts.	Superphosphate and ammonium salts.	Minerals and sodium nitrate.	Superphosphate and sodium nitrate.
Fine gravel, 3-1 mm. ....	23	29	19	12	0.8	19	16	32	33	28	44	33	36	23	34	29	28	26
Grit, 1-0.2 mm. ....	68	72	73	52	54	67	58	52	59	78	71	55	59	55	56	62	70	70
1st sediment .....	23.9	22.7	20.6	21.2	22.4	19.5	18.7	20.2	19.5	17.9	20.6	19.4	20.2	16.9	23.4	21.6	22.6	23.6
2nd " .....	34.7	35.0	31.2	34.7	32.8	33.6	30.2	33.7	35.0	24.8	23.3	27.2	25.6	20.6	28.4	28.2	28.5	27.2
3rd " .....	11.2	9.0	9.6	9.6	9.9	9.3	11.4	10.2	9.7	9.5	12.9	7.5	8.7	12.9	8.7	8.7	9.2	8.1
4th " .....	8.3	6.2	7.3	6.7	6.1	6.6	6.2	7.5	8.0	9.1	9.6	5.6	7.7	11.2	5.7	9.6	5.7	6.0
Klay .....	12.7	14.5	18.0	17.5	18.2	16.6	17.2	16.9	22.9	25.2	17.4	27.6	24.0	13.1	21.6	19.1	18.3	18.6
Moisture .....	2.5	1.7	2.2	1.9	1.8	2.9	2.4	2.8	2.5	2.8	3.4	2.7	3.6	3.7	2.8	2.6	2.1	2.5
Total .....	102.4	99.2	98.1	98.0	97.4	97.1	99.5	101.7	90.5	99.9	98.7	98.8	99.3	95.2	99.6	98.9	96.2	95.0

<i>Separations conducted on raw soil with water only.</i>																		
Fine gravel, 3-1 mm. ....	27	17	23	11	14	22	17	14	26	27	32	34	38	18	37	23	24	37
Grit, 1-0.2 mm. ....	64	73	65	53	55	60	51	48	57	67	53	48	64	47	58	62	66	64
1st sediment .....	21.1	21.3	17.7	24.4	21.5	22.5	21.7	22.9	20.4	20.8	19.6	20.6	19.1	10.7	18.2	19.2	18.2	17.3
2nd " .....	33.3	33.6	32.5	31.6	32.5	31.6	29.6	29.8	24.7	22.3	26.2	29.9	21.8	28.1	28.8	29.7	29.8	31.1
3rd " .....	9.4	8.8	9.0	6.9	10.3	7.6	10.8	8.8	9.2	8.4	9.0	8.0	8.0	9.2	10.4	9.3	10.3	9.0
4th " .....	4.7	4.1	5.6	6.2	5.2	5.1	4.4	4.5	4.4	4.8	5.2	4.1	4.6	5.4	3.6	3.4	5.2	5.2
Klay .....	18.3	17.1	19.1	17.3	17.5	16.5	18.3	20.1	24.5	28.1	20.6	27.4	27.0	20.2	22.8	23.7	17.4	17.8
Loss on solution .....	4.0	4.3	4.8	3.6	3.8	4.4	3.6	4.4	4.5	4.4	4.7	2.8	3.2	3.0	4.1	3.4	4.5	4.3
Moisture .....	2.5	1.7	2.2	1.9	1.8	2.9	2.4	2.8	2.5	2.8	3.4	2.7	3.6	3.7	2.8	2.6	2.1	2.5
Total .....	102.4	99.9	99.7	98.3	99.5	98.8	97.6	99.5	98.5	101.0	97.2	99.7	100.5	98.8	100.2	99.8	96.5	97.3

<i>Separations after washing with acid.</i>																		
Fine gravel, 3-1 mm. ....	27	17	23	11	14	22	17	14	26	27	32	34	38	18	37	23	24	37
Grit, 1-0.2 mm. ....	64	73	65	53	55	60	51	48	57	67	53	48	64	47	58	62	66	64
1st sediment .....	21.1	21.3	17.7	24.4	21.5	22.5	21.7	22.9	20.4	20.8	19.6	20.6	19.1	10.7	18.2	19.2	18.2	17.3
2nd " .....	33.3	33.6	32.5	31.6	32.5	31.6	29.6	29.8	24.7	22.3	26.2	29.9	21.8	28.1	28.8	29.7	29.8	31.1
3rd " .....	9.4	8.8	9.0	6.9	10.3	7.6	10.8	8.8	9.2	8.4	9.0	8.0	8.0	9.2	10.4	9.3	10.3	9.0
4th " .....	4.7	4.1	5.6	6.2	5.2	5.1	4.4	4.5	4.4	4.8	5.2	4.1	4.6	5.4	3.6	3.4	5.2	5.2
Klay .....	18.3	17.1	19.1	17.3	17.5	16.5	18.3	20.1	24.5	28.1	20.6	27.4	27.0	20.2	22.8	23.7	17.4	17.8
Loss on solution .....	4.0	4.3	4.8	3.6	3.8	4.4	3.6	4.4	4.5	4.4	4.7	2.8	3.2	3.0	4.1	3.4	4.5	4.3
Moisture .....	2.5	1.7	2.2	1.9	1.8	2.9	2.4	2.8	2.5	2.8	3.4	2.7	3.6	3.7	2.8	2.6	2.1	2.5
Total .....	102.4	99.9	99.7	98.3	99.5	98.8	97.6	99.5	98.5	101.0	97.2	99.7	100.5	98.8	100.2	99.8	96.5	97.3

TABLE IV.—*Mechanical Analyses of Rothamsted Soils.*

Percentages after ignition to remove organic matter.

Number		1	2	4	25	26	27	Hoos potato, 1903.				Barnfield mangel and grass soils, 1903.																			
		Broadbalk, 1893.		Broadbalk, 1904.		Unmanured.		Dung.		Grass-land.		Minerals and rape-cake.		Dung and rape-cake.		Grass-land.		Minerals and ammonium salts.		Superphos-plate and ammonium salts.		Minerals and sodium nitrate.		Superphos-plate and sodium nitrate.							
		Unmanured.		Minerals and sodium nitrate.		Unmanured.		Minerals and ammonium salts.		Minerals and sodium nitrate.		Dung.		Grass-land.		Minerals and rape-cake.		Dung and rape-cake.		Grass-land.		Minerals and ammonium salts.		Superphos-plate and ammonium salts.		Minerals and sodium nitrate.		Superphos-plate and sodium nitrate.			
Fine gravel, 3—1 mm. ....	2.0	2.6	1.8	0.8	0.7	1.8	1.5	2.5	3.1	2.6	4.2	3.1	3.3	2.0	3.2	2.8	2.6	2.4	2.0	3.2	2.8	2.6	2.4	2.0	2.2	2.0	2.2	2.0	2.2		
Grit, 1—0.2 mm. ....	6.5	7.1	7.1	5.1	5.3	6.5	5.6	4.9	5.7	7.6	6.8	5.3	5.5	5.1	5.5	6.0	6.8	6.8	5.1	5.5	6.0	6.8	6.8	6.8	6.8	6.8	6.8	6.8	6.8		
1st sediment .....	23.6	22.4	20.5	21.1	22.3	19.4	18.5	20.0	19.3	17.8	20.1	19.3	19.9	16.6	23.2	21.4	22.4	22.8	16.6	23.2	21.4	22.4	22.8	22.8	22.8	22.8	22.8	22.8	22.8		
2nd " .....	32.8	34.2	30.9	34.4	32.5	33.2	35.9	34.6	24.5	24.2	22.0	26.9	24.9	28.2	27.9	27.9	28.3	26.9	28.2	27.9	27.9	28.3	26.9	28.3	28.3	28.3	28.3	28.3	28.3		
3rd " .....	10.1	8.7	9.1	9.1	9.5	8.9	11.0	9.5	9.3	8.5	11.0	7.2	7.7	11.6	8.4	8.3	8.7	11.6	7.7	7.7	7.7	8.3	8.7	8.7	8.7	8.7	8.7	8.7	8.7		
4th " .....	6.8	5.5	6.5	5.9	5.7	5.8	5.5	6.0	7.0	7.6	7.9	4.9	5.7	9.3	4.9	8.3	5.0	9.3	4.9	4.9	8.3	5.0	5.4	5.0	5.0	5.4	5.4	5.4	5.4		
Klay .....	10.7	12.3	15.2	15.1	15.4	14.0	14.8	14.9	19.6	21.2	13.5	23.9	20.2	11.1	19.9	16.8	15.6	11.1	19.9	16.8	15.6	17.0	17.0	17.0	17.0	17.0	17.0	17.0	17.0		
Loss on ignition .....	6.8	4.2	5.5	5.8	5.4	5.9	4.5	5.8	4.7	7.7	10.5	5.7	7.8	8.3	4.3	5.2	4.8	8.3	4.3	4.3	5.2	4.8	4.7	4.7	4.7	4.7	4.7	4.7	4.7		
Moisture .....	2.5	1.7	2.2	1.9	1.8	2.9	2.4	2.8	2.5	2.8	3.4	2.7	3.6	3.7	2.8	2.6	2.1	3.7	2.7	2.6	2.1	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5		
Total .....	101.8	98.7	98.8	99.2	98.6	98.4	99.7	101.0	95.7	100.0	99.4	99.0	98.6	95.9	100.1	99.3	96.3	95.9	100.1	99.3	96.3	96.2	96.2	96.2	96.2	96.2	96.2	96.2	96.2	96.2	
<i>Separations after washing with acid.</i>																															
Fine gravel, 3—1 mm. ....	2.5	1.6	2.2	1.0	1.3	2.0	1.6	1.3	2.4	2.5	2.9	3.2	3.5	1.7	3.5	2.2	2.2	1.7	3.5	3.5	2.2	2.2	3.5	2.2	2.2	3.5	3.5	3.5	3.5	3.5	
Grit, 1—0.2 mm. ....	6.2	7.1	6.3	5.2	5.4	5.8	5.0	4.7	5.5	6.3	5.0	4.6	5.8	4.4	5.6	6.1	4.4	4.6	5.8	5.8	6.1	6.5	6.2	6.5	6.5	6.2	6.2	6.2	6.2	6.2	
1st sediment .....	20.8	21.0	17.6	24.3	21.4	22.4	21.5	22.6	20.3	20.6	19.4	20.5	18.8	16.6	18.0	19.0	18.1	16.6	18.0	18.0	19.0	18.1	17.2	18.1	18.1	17.2	17.2	17.2	17.2	17.2	
2nd " .....	32.2	33.3	32.2	31.4	32.3	31.4	29.3	29.3	24.4	22.0	25.3	25.7	24.7	27.5	28.6	29.4	29.3	27.5	28.6	28.6	29.4	29.3	30.6	30.6	30.6	30.6	30.6	30.6	30.6	30.6	
3rd " .....	9.0	8.6	8.7	6.8	10.0	7.4	10.6	8.5	8.9	7.7	8.1	7.7	7.4	8.7	10.1	8.9	10.0	8.7	10.1	10.1	8.9	10.0	8.7	10.0	10.0	8.7	8.7	8.7	8.7	8.7	
4th " .....	3.9	3.6	4.0	5.6	4.6	4.6	4.0	4.0	3.8	3.8	4.2	3.6	3.6	4.5	3.2	3.1	4.7	4.5	3.2	3.1	4.7	4.6	4.6	4.6	4.6	4.6	4.6	4.6	4.6	4.6	
Klay .....	14.7	14.5	16.1	14.9	14.9	13.6	15.6	17.2	22.0	23.6	16.7	23.7	21.6	22.0	19.9	20.5	15.2	22.0	19.9	20.5	15.2	15.2	15.2	15.2	15.2	15.2	15.2	15.2	15.2	15.2	15.2
Loss on solution .....	4.0	4.3	4.8	3.6	3.8	4.4	3.6	4.4	4.5	4.4	4.7	2.8	3.2	3.0	4.1	3.4	4.5	3.2	4.1	3.4	3.4	4.3	4.3	4.3	4.3	4.3	4.3	4.3	4.3	4.3	
Loss on ignition .....	6.8	4.2	5.5	5.8	5.4	5.9	4.5	5.8	4.7	7.7	10.5	5.7	7.8	8.3	4.3	5.2	4.8	8.3	4.3	5.2	4.8	4.7	4.7	4.7	4.7	4.7	4.7	4.7	4.7	4.7	
Moisture .....	2.5	1.7	2.2	1.9	1.8	2.9	2.4	2.8	2.5	2.8	3.4	2.7	3.6	3.7	2.8	2.6	2.1	3.7	2.7	2.6	2.1	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	
Total .....	102.6	99.9	100.5	100.5	100.9	100.4	98.1	100.6	99.0	101.4	100.2	100.2	100.0	100.4	100.1	99.3	97.4	100.4	100.1	99.3	97.4	97.5	97.5	97.5	97.5	97.5	97.5	97.5	97.5	97.5	97.5

A high degree of precision must not be expected from the method, partly because errors due to manipulation readily occur, and even more because of the impossibility of drawing true samples of soil for the analysis, first in the field and then in the laboratory. In the field any slope will mean some variation, whilst every cultivation and every heavy rainfall will to some extent rearrange the physical constitution of the soil. It will be seen, however, that these inevitable variations are never great enough to mask the essential identity of samples drawn from the same area.

The consideration of the results is facilitated if they are recalculated after eliminating the items most subject to variations unconnected with the problem under consideration, that is, the moisture lost at 100°, the loss on solution and ignition, and the coarse material arrested by the sieves, which is too coarse-grained to be accurately distributed in a sample weighing 10 grams only.

The latter fractions constitute only about 10 per cent. of the whole soil and may be dismissed without more consideration in the present case, but they can be determined with accuracy by estimating separately in a sample weighing at least 50 grams.

The figures, however, are not markedly affected by recalculation on such a basis, and it will be sufficient to confine attention to Table IV, in which the varying proportion of organic matter, sometimes high in the finer fractions, has been removed by ignition.

From a consideration of this table the following points will be apparent:

(1) Preliminary treatment with acid results in a greater proportion of "klay" than does the method of working directly on the raw soil, the deficiency in the "klay" fraction in the latter case being generally made up by an increase in the next coarser fraction, and a still smaller increase in the fraction above, the two coarsest fractions being practically identical by both methods.

(2) The differences between the two methods, which are greatest when there is much organic matter in the soil, practically disappear when the soil has been long unmanured, or has been deflocculated by the continued action of saline manures. In the six dunged or grass-land soils, with an average loss on ignition of 7·8 per cent., the proportion of "klay" is 15·3 per cent. when working on the raw soil and increases to 19·3 per cent. after the acid treatment; on the twelve other soils, with an average loss on ignition of 5·1 per cent., the increase is from 16·6 per cent. in the raw soil to 17·2 per cent. as determined after treatment with acid.

(3) Soils which from their proximity we have every reason to consider as identical give similar results by the acid treatment, whatever their manuring has been, but show wide variations when the raw

soil is examined. As a striking example the soils 17, 18, and 24, are all within a few yards of one another in a uniform part of the field, but 18 has been receiving but little organic and much saline manure, 17 has had heavy dressings of organic manures, and 24 has been laid down to grass for many years. By the acid treatment the proportions of "klay" are 21·6, 23·7, and 22·0 per cent. respectively, whilst the raw soil gives 20·2, 23·9, and 11·1 respectively. The acid treatment brings together into one group all the soils of similar origin whatever has been their subsequent management; the results obtained by working on the raw soil depend also on the treatment the land has been receiving. To this conclusion one exception must be made; soils 20, 22, and 27, show a lower proportion of "klay" than the other soils from the same field; this difference, which is a real one, being visible whether the analysis is made on the raw soil or after treatment with acid, will be considered later.

These results lead to the conclusion that the preliminary treatment with acid gives a truer picture of the ultimate physical constitution of the soil than that obtained by working on the raw soil. The acid employed is too weak to cause any reduction in the size of the coarser order of particles such as would bring them within the "klay" limits; were it so, the increased proportion of "klay" due to the acid treatment would not be confined to the soils rich in organic matter, but would be equally manifest with deflocculated soils like 20 and 22, or 19 and 21. These soils give practically identical results by both methods, which is the best evidence that no new error is introduced by the acid treatment. But when working on raw soils well provided with organic matter much of the "klay" is cemented into larger groups by the humus, and these aggregates so far resist the repeated operations of pestling as to be weighed in the coarser fractions. It is not probable that any amount of rubbing up or boiling will completely resolve them, hence the actual amount of "klay" determined will, to some extent, depend on the thoroughness with which these processes are pursued. As however the necessary resolution is fully carried out by the acid treatment, as it also removes all salts capable of causing flocculation, it may be concluded that washing in dilute acid is an essential preliminary to the mechanical analysis of soils.

Further justification is seen in the fact that, when working on the Rothamsted soils, the acid method shows the essential identity of all the soils from the same experimental field, whereas separations made on the raw soils give very dissimilar results, depending on the treatment to which the various plots had been subjected.

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XCVII—*The Effect of the Long-continued Use of Sodium Nitrate on the Constitution of the Soil.*

By ALFRED DANIEL HALL, M.A.

IN the preceding paper attention has been drawn (p. 963) to some exceptions to the general statement there made that soils drawn from different plots in the experimental fields at Rothamsted, showed identical physical constitution whatever treatment the various plots may have received. These exceptional cases showed a relative deficiency in the finest or "klay" fraction and represented soils from plots which received an annual dressing of sodium nitrate. The fact seemed of sufficient importance to demand further examination, so the analyses were extended to include all the Rothamsted fields where a comparison could be obtained between plots receiving (1) sodium nitrate; (2) an equivalent amount of nitrogen in the shape of ammonium chloride and sulphate; (3) a continuously unmanured plot.

In these cases the method of analysis involving a preliminary washing with acid was alone carried out, but the determinations described in the preceding paper show that in dealing with such soils deflocculated by the long use of saline manures, practically the same results would be obtained by working on the raw soil. The results obtained, both as weighed after drying in the steam-oven and after ignition, are set out in Table I, a full description of the soils being given in the preceding paper.

The results show that the plots which have been receiving annual dressings of sodium nitrate contain in general a smaller proportion of "klay" than either the unmanured or the corresponding plots receiving their nitrogen as ammonium salts. The difference is most marked with the mangel field soils, and is not seen at all with the soils from the grass plots in the park. Two explanations of the more coarse-grained structure of the soils from the nitrate plots may be advanced: (1) the loss of the finer particles may be due to the solvent action of the weak solution of sodium nitrate formed in the soil, or (2) it may follow from a washing downwards into the subsoil induced by the deflocculating action of sodium nitrate on the aggregates of "klay" normally existing in the soil. The only support for the former hypothesis lies in the well-known fact that the use of sodium nitrate as a manure does to a large extent enable the crop to obtain potassium from the reserves of this element in the soil; thus by double decomposition the sodium salt does set up chemical change in the finest order of particles (where the potassium of the soil is chiefly

TABLE I.—*Mechanical Analyses of Rothamsted Soils.*  
*Comparison of Soils with and without Sodium Nitrate.*  
*Separations after treatment with acid.*

Number	19	21	20	22	10	11	5	6	7	25	26	27	12	13	14			
	Barnfield, 1903.				Hoos potato, 1903.				Hoos barley, 1904.				Broadbalk, 1904.				The Park, 1904.	
	Minerals and ammonium salts.	Superphos-plate and ammonium salts.	Minerals and sodium nitrate.	Superphos-plate and sodium nitrate.	Ammonium salts.	Sodium nitrate.	Unmanured.	Superphos-plate and ammonium salts.	Superphos-plate and sodium nitrate.	Unmanured.	Minerals and ammonium salts.	Minerals and sodium nitrate.	Unmanured.	Minerals and ammonium salts.	Minerals and sodium nitrate.			
<i>Percentages after drying at 100°.</i>																		
Fine gravel, 3-1 mm.....	3.7	2.3	2.4	3.7	2.3	0.9	3.4	2.2	2.3	1.1	1.4	2.2	2.5	2.2	2.7			
Grit, 1-0.2 mm. ....	5.8	6.2	6.6	6.4	5.6	7.6	7.9	8.1	7.7	5.3	5.5	6.0	2.9	3.5	3.0			
1st sediment .....	18.2	19.2	18.2	17.3	17.6	17.7	20.0	18.1	18.5	24.4	21.5	22.5	17.3	22.1	22.7			
2nd " .....	28.8	29.7	29.8	31.1	30.4	32.4	26.4	27.5	26.1	31.6	32.5	31.6	35.5	33.5	32.4			
3rd " .....	10.4	9.3	10.3	9.0	10.9	11.2	9.9	10.4	9.4	6.9	10.3	7.6	10.4	10.5	8.8			
4th " .....	3.6	3.4	5.2	5.2	5.9	6.1	6.1	5.1	4.8	6.2	5.2	5.1	11.1	5.7	8.1			
Clay ..	22.8	23.7	17.4	17.8	20.3	19.2	18.3	18.3	17.1	17.3	17.5	16.5	16.4	17.2	17.3			
<i>Percentages after ignition.</i>																		
Fine gravel, 3-1 mm.....	3.5	2.2	2.2	3.5	2.1	0.9	3.2	2.1	2.1	1.0	1.3	2.0	2.1	1.9	2.3			
Grit, 1-0.2 mm. ....	5.6	6.1	6.5	6.2	5.5	7.5	7.8	7.7	7.6	5.2	5.4	5.8	2.6	3.1	2.7			
1st sediment .....	18.0	19.0	18.1	17.2	17.5	17.6	20.0	18.0	18.5	24.3	21.4	22.4	17.1	21.8	22.3			
2nd " .....	28.6	29.4	29.3	30.6	30.1	32.1	26.1	27.2	25.9	31.4	32.3	31.4	34.6	32.6	31.6			
3rd " .....	10.1	8.9	10.0	8.7	10.6	10.8	9.5	9.9	9.0	6.8	10.0	7.4	10.1	9.8	8.2			
4th " .....	3.2	3.1	4.7	4.6	5.2	5.4	5.3	4.4	4.2	5.6	4.6	4.6	9.1	4.7	6.6			
Clay ..	19.9	20.5	15.2	15.2	17.7	16.5	15.5	16.4	14.5	14.9	14.9	13.6	12.2	12.7	13.7			

located) and so may lead ultimately to their dissolution. But the chemical change thus brought about would be too small to be appreciable, for the largest amount of sodium nitrate applied—about 12·5 tons per acre during fifty years—bears but a small proportion to the weight of the soil, which amounts to at least 1200 tons per acre for a layer only 9 inches deep.

As regards the other suggested explanation, the fact of deflocculation is very patent in the field; for on the Rothamsted mangel plots, receiving annually heavy dressings of sodium nitrate, the soil retains a larger proportion of water after rain and remains for a long time wet and sticky, eventually drying to a hard cake. These are features characteristic of a fine grained or "clay" soil when the aggregated particles have been resolved into their ultimate particles by "puddling" in a wet condition; although in this case they are associated with the soils containing the smallest proportion of "clay." The existence of the deflocculation in the soil of this field can actually be shown in the laboratory by shaking up small equal weights of soil from the various plots with large volumes of distilled water, and comparing the turbidity after a considerable lapse of time.

It is well known that sodium nitrate in dilute solution, like all salts of strong acids, will flocculate fine particles suspended in a liquid; the cause of its deflocculating action when applied as a manure will be discussed in another place.

To obtain further information on the question as to whether the deficiency in the "klay" fraction in soils from plots receiving nitrate was due to chemical or physical causes, analyses were made of the "klay" itself after separation. The results in the case of the four soils from the mangel field are set out in Table II.

TABLE II.

Analyses of "Klay" fractions \* from Barnfield Soils.

Recalculated to remove constitutional water.

Number of Sample	22	21	20	19
Al <sub>2</sub> O <sub>3</sub> .....	29·27	31·22	29·53	30·33
Fe <sub>2</sub> O <sub>3</sub> .....	12·65	12·86	11·75	12·38
SiO <sub>2</sub> .....	46·42	47·43	47·01	47·96
CaO.....	5·19	4·19	3·54	1·41
MgO .....	1·39	1·58	1·26	1·43
K <sub>2</sub> O.....	2·37	1·88	2·84	3·08
Na <sub>2</sub> O .....	1·14	0·20	2·71	3·19
CO <sub>2</sub> .....	1·57	0·64	1·36	0·22
Total .....	100·00	100·00	100·00	100·00

\* Separated from water only without use of acid.

The analyses show only small differences ; the long use of ammonium salts on Plots 19 and 21 has removed calcium carbonate, calcium has also been removed from 19 and 20 by the use of potassium and magnesium sulphates and sodium chloride, but the variations are small and in no way indicate that the reduction in the weight of the "klay" fraction has been due to the chemical action of sodium nitrate.

An attempt was made to obtain another clue as to the mode of action of the sodium nitrate by determining the proportion of readily decomposable silicates contained in each soil. The samples were subjected to the action of strong hydrochloric acid on the water bath for 48 hours, the acid was washed away and the soluble silica set free by the decomposition of silicates was then extracted by sodium carbonate.

Table III shows that the proportion of silica which could be thus

TABLE III.  
*Percentage of Soluble Silica in Soils.*

No.	Description of soil, &c.	Percentage of residue after extraction with HCl.	Soluble silica per cent. in extracted residue.	Soluble silica per cent. in original soil.
16	Barnfield (1901) Minerals only .....	77.97	11.80	9.20
19	" " Minerals and ammonium salts.....	78.30	13.05	10.22
20	" " Minerals and sodium nitrate.....	80.29	9.25	7.43
10	Hoos potato (1903) Ammonium salts alone	81.43	10.20	8.31
11	" " Sodium nitrate alone.	82.83	8.43	6.98
16	Barnfield (1903) Minerals only .....	78.34	11.75	9.20
19	" " Minerals and ammonium salts.....	79.77	10.65	8.50
20	" " Minerals and sodium nitrate.....	80.66	8.60	6.94
21	" (1901) Superphosphate and ammonium salts.....	86.76	14.4	12.49
22	" " Superphosphate and sodium nitrate .....	78.45	11.1	8.71
	" " Superphosphate, potash, and ammonium salts.....	81.80	14.3	11.70
	" " Superphosphate, potash, and sodium nitrate.....	79.53	9.3	7.40

obtained from each soil, is less from the soils receiving nitrate than from those remaining unmanured or receiving ammonium salts. This only indicates that some of the finest particles composed of hydrated

aluminium silicate have been removed from the soils receiving nitrate, and does not show whether the removal has been effected chemically or physically. However, had the chemical action of the sodium nitrate removed the finest particles it would also have begun to attack the larger particles of hydrated silicate, thus exposing them to decomposition on treatment with the strong hydrochloric acid as described above. On the whole this line of evidence points to the physical removal of the fine particles from the soils receiving nitrate.

Lastly, evidence may be obtained from the subsoils. Table IV shows the analyses of the subsoils of the three plots in the wheat field which have been already considered, and from them it will be seen that the amount of "klay" although less in the surface soil is greater in the subsoil where sodium nitrate has been annually applied. Clearly the more turbid waters percolating from the surface soils of the sodium nitrate plot have been filtered in the subsoil, and some of the fine suspended matter has been retained until its accumulation has become appreciable. That the arrest of the finest material in the subsoil is not quite complete may be gathered from another fact. A tile drain is situated beneath each of the plots just mentioned in the wheat field at a depth of about 30 inches, the drains all debouch into a cross trench at the bottom of the field, and records are kept of the occasions on which each drain runs. For many years even in the winter months the drain beneath the unmanured plot ran more freely than that beneath the plot receiving sodium nitrate. Gradually, as deflocculation has taken effect, and the finest particles have been washed out of the soil of the nitrate plot above the drain, percolation has become more rapid until during the last ten years, a period subsequent to the drawing of the subsoil samples analysed, the drain of the nitrate plot has run the more frequently of the two. It is also noticed that the water running from this drain is perceptibly more turbid than that from the neighbouring drains.

Table V shows a comparison of the number of times the drains beneath these two plots run in the winter months (the other months must be excluded because of the drying effect of the greater crop on the nitrate plot).

Deflocculation followed by the washing down of the finest particles would also explain the differences observed in the effect of sodium nitrate on the proportion of "klay" in the soils of the different fields. The loss of "klay" is most evident in the case of the mangel field, where large amounts of sodium nitrate (550 lb. per acre per annum) are used and the land receives continual cultivation during the greater part of the year, so that the surface soil is always in a condition to allow the rain to percolate freely through it. On the wheat field a smaller amount of nitrate is applied and the cultivation is con-

TABLE IV.—*Mechanical Analyses of Soils and Subsoils, Broadbalk Field, Rothamsted.**Percentages after Treatment with Acid.*

	Unmanured.		Minerals and ammonium salts.		Minerals and sodium nitrate.	
	Dried at 100° C.	Ignited.	Dried at 100° C.	Ignited.	Dried at 100° C.	Ignited.
<i>First depth, 0—9 inches.</i>						
Fine gravel, 3—1 mm.....	1·1	1·0	1·4	1·3	2·2	2·0
Grit, 1—0·2 mm .....	5·3	5·2	5·5	5·4	6·0	5·8
1st sediment.....	24·4	24·3	21·5	21·4	22·5	22·4
2nd „ .....	31·6	31·4	32·5	32·3	31·6	31·4
3rd „ .....	6·9	6·8	10·3	10·0	7·6	7·4
4th „ .....	6·2	5·6	5·2	4·6	5·1	4·6
“ Klay ”.....	17·3	14·9	17·5	14·9	16·5	13·6
<i>Second depth, 10—18 inches.</i>						
Fine gravel, 3—1 mm.....	1·9	1·7	1·3	1·2	2·0	1·7
Grit, 1—0·2 mm .....	4·7	4·6	4·0	4·0	4·1	4·0
1st sediment.....	17·3	17·2	16·4	16·3	13·7	13·7
2nd „ .....	23·7	23·5	24·9	24·7	23·5	23·3
3rd „ .....	12·0	11·8	8·5	8·2	11·1	10·9
4th „ .....	6·3	5·8	5·5	4·9	6·8	6·0
“ Klay ”.....	26·6	23·2	29·2	25·7	30·2	26·5
<i>Third depth, 19—27 inches.</i>						
Fine gravel, 3—1 mm.....	0·3	0·2	0·5	0·5	0·7	0·7
Grit, 1—0·2 mm .....	1·5	1·4	3·3	3·2	2·8	2·7
1st sediment.....	12·5	12·5	16·6	16·6	10·6	10·5
2nd „ .....	20·1	20·0	17·8	17·7	16·1	16·0
3th „ .....	11·4	11·1	8·9	8·7	8·1	7·9
4th „ .....	4·5	4·1	3·9	3·5	4·6	4·2
“ Klay ”.....	38·8	34·2	38·2	34·3	43·1	38·9

fined to about a month in the late autumn, after which the land lies in a moderately firm condition. The barley field also gets but little working although rather more than the wheat field, the potato land more nearly resembles the mangel field. In each of these cases the

TABLE V.

*Number of Days on which the Drains ran. Broadbalk Field, Rothamsted.*

Five-year periods.	Whole year.		Dec., Jan., and Feb.	
	Unmanured.	Sodium nitrate.	Unmanured.	Sodium nitrate.
1866/7 to 1870/71	43	38	32	35
1871/2 „ 1875/6	64	53	29	27
1876/7 „ 1880/1	111	92	44	40
1881/2 „ 1885/6	115	87	54	46
1886/7 „ 1890/1	72	77	29	32
1891/2 „ 1895/6	98	103	46	49
1896/7 „ 1900/01	78	120	44	71

removal of “klay” from the surface soil is less than on the mangel field. On the other hand the grass-land gets no stirring of the soil at all, and percolation, owing to the covering of grass, is reduced both in quantity and speed; here only is there no falling off in the proportion of “klay” in the soil of the plots receiving sodium nitrate as compared with the soil of the other plots, and this notwithstanding the large amount of the salt used. Had the action of the nitrate in reducing the proportion of “klay” been a chemical one, the effect would have been as great on the grass-land plots as anywhere else.

These results show what difficulties are encountered in the interpretation of mechanical analyses; the soils receiving sodium nitrate are constituted of coarser grains, and possess a smaller proportion of “klay,” yet because of their extreme state of deflocculation they behave in the field as if they contained an exceptionally high proportion of the finest particles. Both the methods of analysis under discussion would fail to detect the deflocculation, so rendering it impossible to predict the actual texture of the soil from the measurements of the particles. The results, however, when working on the raw soil, would be to some extent affected by the deflocculation, and thus an element of uncertainty would be introduced. For example, when working on the raw soil, Nos. 21 and 22 show very similar results, namely, about 17 per cent. of ignited “klay”; but by the acid treatment No. 21 gives 20·5 per cent. of “klay” as against 15·2 per cent. in No. 22. Neither of these results accords with the observed texture of the soil at the time the samples were taken, but the acid treatment brings to light a fact, namely, the removal of the

"klay" from nitrated soils, which would be left obscure if the analysis had been made on the untreated soil.

*Summary and General Conclusions.*

By the mechanical analysis of soils from the five experimental fields at Rothamsted, on which there are plots manured with sodium nitrate, it is found that the soil of these plots generally contains a lower proportion of the finest "klay" fraction than does the soil of adjoining plots which have been either unmanured or have received ammonium salts in place of sodium nitrate. This result was most manifest in the mangel field where cultivation is frequent, and was not apparent at all in the grass field where the turf protects the soil from the washing action of the rain.

The removal of the finest particles from the surface soil is attributed to deflocculation induced by the use of sodium nitrate, and followed by the washing of the finest particles into the subsoil. This hypothesis is confirmed by chemical analyses of the "klays" separated in the mechanical analysis, by the examination of some of the subsoils, which are found to be richer in fine particles beneath the soils receiving nitrate, and by the condition of the soils in the field, which show every evidence of deflocculation.

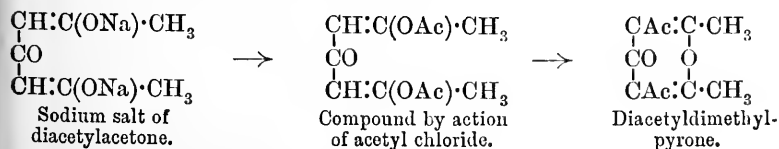
THE ROTHAMSTED EXPERIMENTAL STATION,  
HARPENDEN.

*XCVIII.—The Action of Acetyl Chloride on the Sodium Salt of Diacetylacetone, and the Constitution of Pyrone Compounds.*

By JOHN NORMAN COLLIE, F.R.S.

THE following investigation was made in order to find out whether by the introduction of acetyl groups into dimethylpyrone, its power of forming salts with acids would be affected.

In order to prepare diacetyldimethylpyrone, the same reaction was employed as in the production of tetramethylpyrone (Collie and Steele, *Trans.*, 1900, 77, 962).



In the first two preparations, a compound melting at  $124^{\circ}$  was obtained, which seemed to be identical with a substance made from the copper derivative of acetylacetone and carbonyl chloride by Thomas and Lefèvre (*Bull. Soc. chim.*, 1889, 50, 193—194). It was therefore considered to be diacetyldimethylpyrone. However, on attempting to prepare more of the compound; instead of the foregoing substance (m. p.  $124^{\circ}$ ) being obtained, the chief product melted at  $94^{\circ}$ . Another experiment was therefore made and every precaution taken to have all the reacting substances pure and dry, the temperature being also kept below  $0^{\circ}$  whilst the reaction was taking place between the sodium salt and acetyl chloride. Under these conditions, a substance melting at  $75^{\circ}$  resulted.

These three compounds were isomeric, having a composition expressed by the formula  $C_{11}H_{12}O_4$ . The compound melting at  $124^{\circ}$  seemed undoubtedly to be a pyrone derivative; it gave no reaction with ferric chloride, could be sublimed easily, and furnished a yellow precipitate when boiled with excess of barium hydroxide.

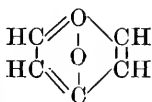
The compound melting at  $95^{\circ}$  gave all the reactions of a benzene metadihydroxy-derivative. With ferric chloride, it developed a purple coloration; its solution in chloroform and sodium hydroxide had a bright red colour, which, on dilution with water, became green and fluorescent, whilst with phthalic anhydride and sulphuric acid a dye was obtained which gave a deep red solution with alkalis.

The third substance, melting at  $75^{\circ}$ , was found to be capable of transformation either into the pyrone compound (m. p.  $124^{\circ}$ ) when boiled with hydrochloric acid or into the benzene derivative (m. p.  $95^{\circ}$ ) when boiled with sodium hydroxide; it also developed a purple coloration with ferric chloride.

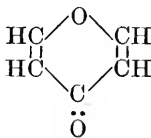
If the commonly accepted formulæ for diacetylacetone and dimethylpyrone be used, it will be found difficult to explain the existence and formation of these compounds. The view that the accepted formula for dimethylpyrone is at variance with the properties of that substance is not now brought forward for the first time.

In 1891 (*Ber.*, 24, 2450), Brühl says: "Although Claissen's synthesis of chelidonic acid affords evidence in favour of the pyrone formula  $CO<\begin{smallmatrix} CH:CH \\ CH:CH \end{smallmatrix}>O$ , first proposed by Lieben and Haitinger, yet, as pyrone does not form additive compounds or a hydrazone or an oxime, further confirmation seems desirable." The author has for a long time held the same view, but it is only lately that facts have been obtained which justified the adoption of another formula, seemingly more in harmony with the properties and reactions of pyrone derivatives. Its adoption was mainly due to the evidence obtained from

the absorption spectra and refractive indices of a large number of pyrone compounds.\*



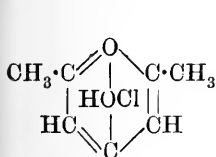
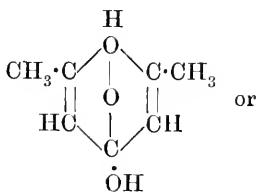
New formula.



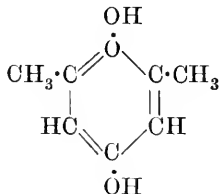
Lieben and Haitinger's formula.

Such a substance would behave as a saturated compound. Like benzene, it would be difficult to reduce, and would form neither an oxime nor a hydrazone. The presence of one oxygen atom combined in a way unknown amongst ordinary oxygen compounds might be taken as a reason why pyrone and dimethylpyrone so readily form salts with acids. Such a formula also is not opposed to the facts that dimethylpyrone is not attacked either by nitric or sulphuric acid, neither can it be hydrogenated by ordinary reducing agents. This compound is, in fact, a remarkably stable and inert substance.

If the new formula for dimethylpyrone be accepted, then the following formulæ will express the molecular structure of some of its derivatives :

Dimethylpyrone  
hydrochloride.

Diacetylacetone.



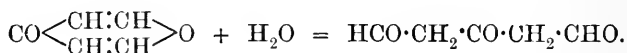
These formulæ for diacetylacetone agree well with the observed properties of the substance, and they account for its very high refractive index, which is almost equal to that of benzene.

The molecular refractive indices of both diacetylacetone and dimethylpyrone are abnormally high, being 39.99 and 35.34, whilst the calculated numbers for two compounds, having the ordinary formulæ,  $\text{CO} \langle \text{CH}:\text{C}(\text{CH}_3) \rangle \text{O}$  and  $\text{CH}_3 \cdot \text{C}(\text{OH}) : \text{CH} \cdot \text{CO} : \text{CH} : \text{C}(\text{OH}) \cdot \text{CH}_3$ , would be 34.88 and 33.30 respectively.

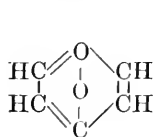
Experiments have also been carried out with pyrone, which tend to

\* The measurement of the refractive indices and the absorption spectra of a large number of pyrone compounds has lately been carried out under the author's direction, and it is hoped that they will soon be published.

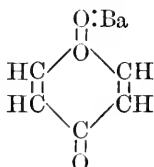
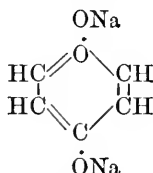
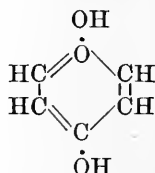
prove that in no case is it likely that open chain compounds are produced. For instance, pyrone in dilute aqueous solution, when warmed with barium hydroxide, gives a yellow barium salt and forms, with sodium hydroxide, a colourless sodium salt; both these substances, when dissolved in dilute hydrochloric acid solution, develop a stable, deep blood-red coloration with ferric chloride solution. This result is hardly to be expected from the dialdehyde of acetonedicarboxylic acid.



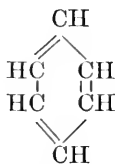
The new formula for pyrone, however, would represent these substances as follows :



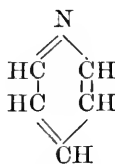
Pyrone.

Barium salt  
(yellow).Sodium salt  
(colourless).Substance produced  
by the action of  
hydrochloric acid on  
sodium salt.

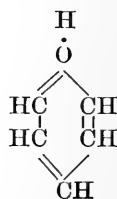
In this connection, it is worth while pointing out that the last compound is the dihydroxy-derivative of a hypothetical substance which is the oxygen analogue of pyridine, and might therefore be termed *oxene*.



Benzene.



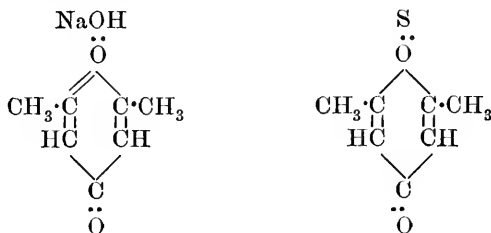
Pyridine.



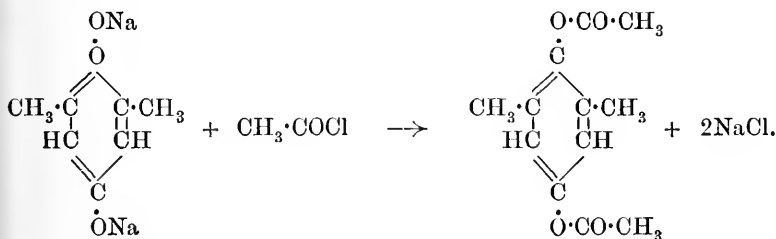
Oxene.

Diacetylacetone would therefore be *dihydroxydimethyloxene*. Several attempts have been made to obtain a quinone by oxidation of diacetylacetone, but without much success, for the compound loses water very easily, giving dimethylpyrone. There are, however, two reactions by which bright coloured substances are formed. If solid sodium hydroxide is powdered in a mortar with crystals of dimethylpyrone, a brilliant pink coloration is developed, which is, however, destroyed on the addition of water. Also sulphur, when heated with dimethylpyrone, gives rise to a bright red compound. In these reac-

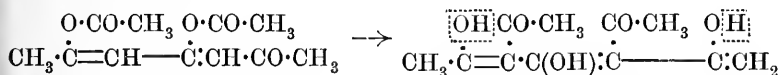
tions, quinonoid compounds of the following composition might be formed :



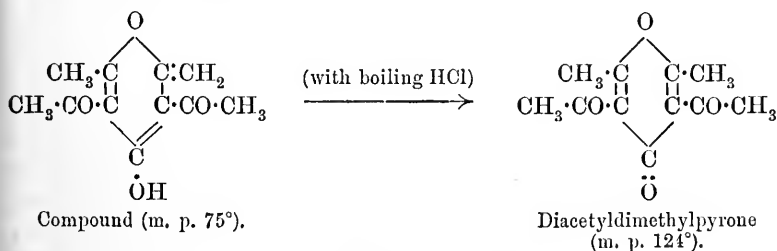
An explanation can now be given of the constitution of the three compounds,  $\text{C}_{11}\text{H}_{12}\text{O}_4$ , formed by the action of acetyl chloride on the sodium salt of diacetylacetone :



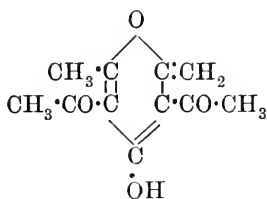
Rearrangement with the elimination of water then takes place, and this change is possibly due to the intermediate formation of an open chain compound :



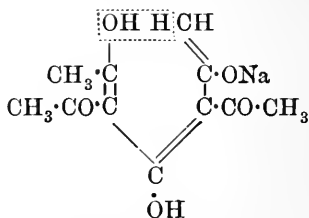
the latter then giving rise to a closed ring derivative by the elimination of water :



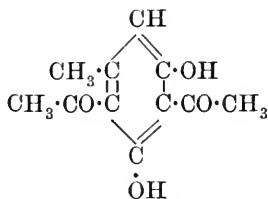
The formation of an orcinol derivative by the action of sodium hydroxide on the compound (m. p. 95°) may be represented as follows :



Compound (m. p. 75°).



Intermediate compound.



Diacetylorscinol.

## EXPERIMENTAL.

When diacetylacetone is dissolved in absolute alcohol and a solution of sodium ethoxide added, a crystalline precipitate of the disodium salt is at once produced. A hydrated form of the same salt can also be made by adding sodium ethoxide to a solution of dimethylpyrone in about 95 per cent. alcohol. In the following experiments, the sodium salt was made by both of these methods, but was, however, always heated under diminished pressure on a water-bath until free from alcohol and any water of crystallisation, before it was suspended in chloroform and subjected to the action of acetyl chloride.

An analysis of the dried sodium salt thus made from dimethylpyrone gave Na=22.6 per cent., whereas  $\text{C}_7\text{H}_5\text{O}_3\text{Na}, \text{H}_2\text{O}$  requires 22.6. During the first experiments, the temperature of the mixture was allowed to rise as the somewhat violent reaction took place, and was only cooled when the chloroform began to boil.

When all the acetyl chloride had been added, the mixture was diluted with water, and the chloroform layer separated and evaporated; the residue was then boiled with water until nearly all dissolved, a small quantity of oily matter being left. The crystals deposited by the aqueous solution on cooling, melted at 124° after purification. The mother liquor contained a considerable amount of dimethylpyrone, and as a result the yield of the substance melting at 124° was only about 20 per cent. of the theoretical amount.

On trying with larger quantities of the sodium salt and acetyl chloride, the insoluble oil was formed in much larger amount, being the chief substance produced. This product slowly crystallised, and

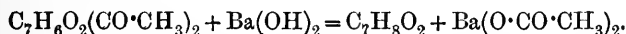
when purified by recrystallisation from dilute alcohol and boiling with animal charcoal, it then melted at  $95^{\circ}$ , and differed obviously from the compound obtained in the first experiments.

*Compound* (m. p.  $124^{\circ}$ ).—This substance, which seems identical with that obtained by Thomas and Lefèvre (*loc. cit.*), is slightly soluble in cold water, but more so in the hot solvent or in alcohol; it sublimes at  $100^{\circ}$ , forming glistening plates, and boils with decomposition above  $300^{\circ}$ .

	Found.		Calculated.
	I.	II.	$C_{11}H_{12}O_4$ .
C .....	63.2	63.0	63.4
H .....	6.0	5.7	5.8

It does not develop a coloration with a ferric chloride solution, and is therefore diacetyldimethylpyrone. When boiled with barium hydroxide, it gives, somewhat slowly, a yellow insoluble barium salt, which was found to be, not the barium salt of diacetyldimethylpyrone, but that of dimethylpyrone; for when dissolved in dilute hydrochloric acid it gave diacetylacetone (m. p.  $54^{\circ}$ ), and after boiling with somewhat stronger acid yielded the hydrochloride of dimethylpyrone. From this salt, dimethylpyrone (m. p.  $132^{\circ}$ ) was made, and also a specimen of its platinichloride,  $(C_7H_8O_2)_2, H_2PtCl_6$ .

Barium acetate was found in the aqueous solution and the reaction therefore is as follows :



Diacetyldimethylpyrone possesses the remarkable property of assuming a brilliant lemon-yellow colour when exposed either to sunlight or to the light of the electric arc between iron poles. The colourless variety is at once regenerated when the yellow substance is melted or dissolved in any solvent. On account of this instability, the molecular complexity of the yellow compound, which also melted at  $124^{\circ}$ , could not be determined. Diacetyldimethylpyrone was found to be apparently without basic properties; its solution in hot hydrochloric acid, when allowed to evaporate spontaneously, yielded not a trace of hydrochloride, and no double salt could be obtained with platinic chloride. From these properties, and also on account of its relatively low specific refraction, it does not seem to contain a quadrivalent oxygen atom.

*Compound* (m. p.  $95^{\circ}$ ).—This substance, on analysis, proved to be isomeric with diacetyldimethylpyrone.

	Found.		Calculated.
	I.	II.	$C_{11}H_{12}O_4$ .
C .....	62.8	63.0	63.4
H .....	6.1	5.7	5.8

As, however, it developed a purple coloration with ferric chloride, and when heated with phthalic anhydride or with sodium hydroxide and chloroform gave reactions similar to those of orcinol, it was considered to be a benzene derivative.

When boiled with barium hydroxide, it gives a yellow solution, from which hydrochloric acid reprecipitates the original compound; with sodium hydroxide, it behaves in a similar manner. It remains unchanged when evaporated with hydrochloric acid, but dissolves in strong sulphuric acid to an intensely yellow solution, from which it is reprecipitated on the addition of water.

That the compound is an orcinol derivative was proved in the following manner: 2 grams of the substance were dissolved in 4 c.c. of strong sulphuric acid, 4 drops of water were added, and the mixture heated to  $130^{\circ}$ . The yellow colour disappeared, an odour of acetic acid was noticed, and no insoluble compound was precipitated on adding more water; the solution was neutralised with sodium carbonate, extracted with ether several times, and the ethereal solution evaporated to dryness. The residual syrup, on distillation, boiled at  $290\text{--}300^{\circ}$ , and the crystalline distillate was found to be pure orcinol. When heated with acetic anhydride, it yielded an acetyl derivative melting at  $75^{\circ}$ .

	Found.	Calculated.
		$C_{11}H_{11}O_4 \cdot CO \cdot CH_3$ .
C .....	62.4	62.4
H .....	5.6	5.6

If bromine water is added to a solution of the compound (m. p.  $95^{\circ}$ ) in dilute acetic acid, a dense, yellow precipitate is obtained, which is also produced by adding excess of bromine to a solution of the compound in glacial acetic acid. After successive crystallisations from acetic acid and dilute alcohol, the bromo-derivative melted at  $79^{\circ}$ . On analysis, it gave Br = 27.8 per cent., whereas  $C_{11}H_{11}O_4Br$  requires 27.9.

The substance (m. p.  $95^{\circ}$ ) is therefore a diacetyldihydroxymethylbenzene. At first it was not obvious why the action of acetyl chloride on the sodium salt of diacetylacetone should, in the one case, lead to the production of a pyrone compound, whilst in another experiment performed under almost exactly similar conditions, the chief product of the reaction should be a benzene derivative. It is true that in neither reaction was the yield much more than about 20 per cent. of the calculated amount, but as water was also one of the products of the reaction, this would at once decompose the acetyl chloride, forming hydrochloric and acetic acids, and these in their turn would then convert the sodium salt of diacetylacetone into dimethylpyrone, sodium acetate, sodium chloride, and more water. In order to eliminate these

secondary reactions as far as possible, some further experiments were made, in which the substances were as dry and as pure as possible.

The sodium salt was made from diacetylacetone and sodium ethoxide in absolute alcohol; it was then carefully washed and dried under diminished pressure at  $100^{\circ}$ . The chloroform was dried over phosphoric oxide and the acetyl chloride distilled and purified as far as possible from hydrochloric acid. Moreover, during the addition of acetyl chloride to the sodium salt suspended in chloroform, the temperature was kept below  $-15^{\circ}$ . After all the acetyl chloride had been added, the sodium salt, which was quite insoluble in the chloroform, had entirely dissolved to a clear solution, no sodium chloride having been formed. But when this clear solution was taken out of the freezing mixture and the temperature allowed to rise, at about  $0^{\circ}$  the whole product set to a transparent, thick jelly which gradually became opaque, finally settling down to the bottom of the flask as a precipitate of ordinary sodium chloride. It is noteworthy that sodium chloride, when precipitated from an absolutely dry chloroform solution, should separate as an apparently colloidal substance. In order to separate the sodium chloride, water was added to the mixture and the whole neutralised with sodium hydroxide, the chloroform solution being then separated and evaporated. The residue, after washing with a little water to remove dimethylpyrone, was purified by solution in hot dilute alcohol, and decolorised by animal charcoal. The pure compound melted at  $75^{\circ}$ , and on analysis was also found to have the composition  $C_{11}H_{12}O_4$ .

	Found.		Calculated.
	I.	II.	$C_{11}H_{12}O_4$ .
C.....	63.0	63.4	63.4
H.....	5.8	5.7	5.8

That the compound contained a hydroxyl group was proved by the fact that it developed a deep purple coloration with ferric chloride. The most interesting property possessed by this substance, however, was its remarkable faculty for undergoing isomeric change when treated with acids or alkalis. When boiled with acids, especially hydrochloric acid, it changed into the pyrone derivative (m. p.  $124^{\circ}$ ), and on warming with sodium hydroxide it was transformed into the benzene derivative (m. p.  $95^{\circ}$ ). These results explained why, under one set of conditions, the chief product of the reaction between acetyl chloride and the disodium salt of diacetylacetone was diacetyldimethylpyrone, whilst under another set the benzene compound (m. p.  $95^{\circ}$ ) was formed in greater quantity.

The author hopes, before long, to bring forward several other cases illustrating this property possessed by diacetylacetone derivatives of easily condensing to form orcinol compounds. The reaction is of im-

portance because many essential principles in plants contain a *m*-dihydroxybenzene residue. Moreover, by further hydrolytic condensation of orcinol with acetylacetone and diacetylacetone, a series of coloured compounds is easily produced, and therefore as has been shown by the author in some earlier papers on diacetylacetone, not only benzene, naphthalene, *isoquinoline*, and pyridine derivatives, but also compounds similar to fisetin and other non-nitrogenous vegetable colouring matters can be built up by the simplest reactions from acetic acid.

The author wishes to take this opportunity of thanking the Chemical Society for a grant towards the expense of this research.

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### XCIX.—*Note on the Hydrolysis of Starch by Diastase.*

By JOHN SIMPSON FORD.

IN Kjeldahl's classical researches (*Compt. rend., Carlsberg*, 1879, 1, 2, 118) on diastatic action, he stated his "law of proportionality" as follows. "Le rapport entre la teneur en diastase (pouvoir fermentatif) de deux dissolutions d'extrait de malt peut être exprimé par le pouvoir réducteur qu'elles produisent lorsqu'elles agissent toutes les deux sur un même poids d'amidon à la même température et pendant le même temps, le pouvoir réducteur ne dépassant pas 25—30." \* The experiments, detailed in the French *résumé*, were made with extracts from kiln-dried malt, and, although it is fairly obvious from the internal evidence of the paper that he had satisfied himself that the "law" held also for air-dried malt and barley, no experimental evidence is given to prove this. In some experiments made several years ago on the distribution of diastase in germinating barley, the author obtained such concordant results in the determination of the amounts of diastase in whole corns and in portions thereof as to show that the "law" was applicable to the diastase of barley and air-dried malt. Brown and Morris, in their important researches on the "Germination of the *Gramineæ*" (*Trans.*, 1890, 57, 507), had already given the same indirect confirmation.

In a paper on "Malt analysis" (*J. Fed. Inst. Brewing*, 1902, 8, 445), Ling states that the "law" does not hold for the diastase of air-dried

\* The reducing power is here expressed in terms of dextrose.

malt, and gives some experimental data in support of this statement. As this is a matter of considerable importance, the writer has made experiments with extracts from various barleys and air-dried malts,\* the results of which show that the law of proportionality enunciated by Kjeldahl is true for the diastase (amylase) in extracts of barley and air-dried malt as well as for that in extracts of kiln-dried malt.

In a recent communication on "Lintner's soluble starch and the estimation of 'diastatic power'" (J. S. Ford, *J. Soc. Chem. Ind.*, 1904, 23, 414), attention was drawn to the influence of slight traces of impurities on amylolytic action, and it is probable that the discrepant results obtained by Ling and the author are due to the use of starches of different degrees of purification. The substances other than amylase in the extracts of malt or grain may also influence the results to an extent dependent on the nature and amount of the impurities in the starch solutions.

Two different preparations of Lintner's soluble starch used in the experiments recorded below were tested with colour indicators, when 10 grams of each required the following amounts of standard solutions :

	A.	B.
Rosolic acid, c.c. $N/100$ $H_2SO_4$ .....	neutral	1.5
Phenolphthalein, c.c. $N/100$ $NaOH$ .....	18.0	19.0

Both starches gave the same amount of maltose with equal volumes of extracts under the same conditions of time and temperature, and yielded similar results as regards "proportionality" with extracts of barley and high and low dried malts. For these experiments, the extracts were obtained by shaking for 1 hour in a special machine 20 or 25 grams of finely ground barley or malt with 500 c.c. of distilled water, filtering rapidly, and employing the solution immediately.

A preliminary experiment was made to determine the activity of the extract, which was then further diluted when necessary, so that the maximum production of maltose would fall somewhere about the limits of the "law of proportionality," corresponding with a reducing power  $R$  of about 40 per cent. of maltose on the starch solids. Brown and Glendinning (*Trans.*, 1902, 81, 398) have recently pointed out that Kjeldahl's law, as shown by his own results, is approximately correct when the  $R$  of the solution does not exceed 30—40, and the trend of the results given below is in agreement with this. The quantities of the extracts were added to 70 c.c. of starch solution at the desired temperatures, the action being stopped at the expiry of 1 hour by the addition of caustic soda. The solutions were then diluted to 100 c.c. at  $15.6^\circ$ , and their copper-reducing power determined

\* Dried at  $17-40^\circ$ .

by the method employed by Brown, Morris, and Millar; the results were corrected for the reduction due to the starch solution and extract. In the following tables,  $E$  = the volume (c.c.) of the barley or malt extract;  $M$  = maltose produced in grams per 100 c.c.;  $R$  = maltose per cent. on starch solids, allowance being made for the increase due to hydration of starch;  $R/E$  is a constant up to  $R = 30-40$  if Kjeldahl's law holds.

Considering the fairly large experimental errors of such work and the known influence of minute traces of impurity on amylolytic action, the author is of opinion that his results show clearly that the amylase in extracts of air-dried malt and barley conforms to the "law of proportionality." How far pure amylase acting on pure starch would do so has yet to be shown, but for analytical purposes it is obvious that the approximation is sufficiently close.

TABLE I.

*Transformations with Extracts from Air-dried Malt.*

$E$ .	$M$ .	$R$ .	$R/E$ .	$E$ .	$M$ .	$R$ .	$R/E$ .
16°.				40°.			
<i>Starch, 2.55 grams.</i>				<i>Starch, 2.55 grams.</i>			
0.5	0.045	1.8	3.6	0.25	0.050	2.0	8.0
1.0	0.091	3.6	3.6	0.5	0.104	4.1	8.2
2.0	0.174	6.8	3.4	1.0	0.212	8.3	8.3
3.0	0.260	10.2	3.4	2.0	0.419	16.4	8.2
4.0	0.347	13.6	3.4	3.0	0.637	24.9	8.3
5.0	0.430	16.8	3.4	4.0	0.827	32.3	8.1
6.0	0.512	20.0	3.3	5.0	1.001	39.0	7.8
7.0	0.597	23.3	3.3	6.0	1.150	44.7	7.4
8.0	0.675	26.3	3.3				
9.0	0.754	29.4	3.2				
10.0	0.830	32.4	3.2				
11.0	0.905	35.3	3.2				
20°.				56°.			
<i>Starch, 1.50 grams.</i>				<i>Starch, 1.50 grams.</i>			
0.5	0.100	6.7	13.4	0.5	0.124	8.3	16.6
1.0	0.198	13.2	13.2	1.0	0.244	16.2	16.2
1.5	0.301	20.0	13.3	1.5	0.363	24.1	16.1
2.0	0.384	25.5	12.7	2.0	0.495	32.3	16.4
2.5	0.448	29.7	11.9	3.0	0.687	45.4	15.1
3.0	0.517	34.3	11.4				

TABLE II.

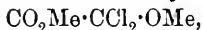
*Transformations with Extracts from Barley.*

<i>E.</i>	<i>M.</i>	<i>R.</i>	<i>R/E.</i>	<i>E.</i>	<i>M.</i>	<i>R.</i>	<i>R/E.</i>
15°.				40°.			
<i>Starch, 2.00 grams.</i>				<i>Starch, 2.00 grams.</i>			
1	0.138	6.9	6.9	1	0.082	4.1	4.1
2	0.277	13.8	6.9	2	0.174	8.7	4.4
4	0.556	27.7	6.9	3	0.252	12.6	4.2
6	0.791	39.3	6.5	4	0.320	16.0	4.0
8	0.955	47.3	5.9	5	0.411	20.5	4.1
10	1.074	53.2	5.3	6	0.488	24.3	4.0
16°.				8	0.661	32.8	4.1
<i>Starch, 1.95 grams.</i>				10	0.790	39.2	3.9
1	0.025	1.3	1.3	56°.			
2	0.049	2.5	1.3	<i>Starch, 2.00 grams.</i>			
3	0.073	3.7	1.2	0.5	0.064	3.2	6.4
4	0.097	5.0	1.3	1.0	0.128	6.4	6.4
5	0.124	6.4	1.3	1.5	0.193	9.6	6.4
6	0.145	7.4	1.2	2.0	0.256	12.8	6.4
7	0.172	8.8	1.3	2.5	0.316	15.8	6.3
8	0.204	10.4	1.3	3.0	0.380	18.9	6.3
10	0.245	12.5	1.3	4.0	0.502	25.0	6.2
20°.				5.0	0.620	30.8	6.1
<i>Starch, 2.00 grams.</i>							
0.5	0.025	1.3	2.6				
1.0	0.049	2.5	2.5				
2.0	0.097	4.9	2.5				
4.0	0.200	10.0	2.5				
6.0	0.301	15.0	2.5				
8.0	0.402	20.0	2.5				
10.0	0.491	24.5	2.5				

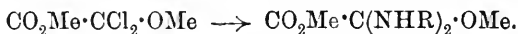
C.—*Imino-ethers and Allied Compounds Corresponding with the Substituted Oxamic Esters.*

By GEORGE DRUCE LANDER.

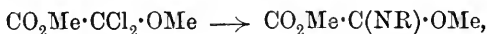
ANSCHÜTZ AND STIEPEL (*Ber.*, 1895, 28, 60; *Annalen*, 1899, 306, 5) have described the condensation of methyl dichloro-oxalate,



with piperidine, phenyl hydrazine, aniline, and *p*-toluidine, and their results may be briefly expressed as follows: when piperidine, aniline, or *p*-toluidine act on the dichloro-ester in cold absolute ethereal solution, diamido-compounds are formed as indicated by the scheme:



When aniline and *p*-toluidine act on the dichloro-ester in warm xylene solution, imino-ethers are formed,

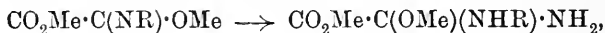


whilst phenylhydrazine either in cold or warm solution yields the imino-ether,  $\text{CO}_2\text{Me}\cdot\text{C}(\text{N}\cdot\text{NHPh})\cdot\text{OMe}$ .

On allowing the aniline and *p*-toluidine diamido-compounds to remain in contact with cold dilute hydrochloric acid, the same imino-ethers are formed by loss of one molecule of arylamine,



The arylimino-ethers take up the elements of ammonia at the ordinary temperature, yielding mixed ortho-compounds,



a behaviour which the authors consider characteristic of the imino-ethers.

The physical and chemical properties of Anschütz and Stiepel's semi-*N*-arylimino-oxalic dimethyl ethers,  $\text{CO}_2\text{Me}\cdot\text{C}(\text{NPh})\cdot\text{OMe}$  and  $\text{CO}_2\text{Me}\cdot\text{C}(\text{N}\cdot\text{C}_7\text{H}_7)\cdot\text{OMe}$ , are totally different from those of the semi-*N*-phenylimino-oxalic diethyl ether,  $\text{CO}_2\text{Et}\cdot\text{C}(\text{NPh})\cdot\text{OEt}$  (*Trans.*, 1901, 79, 699).

It seemed possible that the imino-ethers obtained from the dichloro-ester might be the geometrical isomerides of those obtainable from the substituted oxamates by means of alkylation with silver oxide and alkyl iodides, and I therefore thought it desirable to prepare semi-*N*-phenylimino-oxalic dimethyl ether from methyl oxanilate by silver oxide methylation, and to compare this ether with the substance procured from the dichloro-ester and aniline.

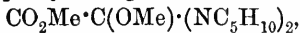
The properties of the two compounds are compared in the following table.

Imino-ether of Anschütz and Stiepel.	Imino-ether from methyl oxanilate.
Solid.	Liquid.
M. p. 111°.	B. p. 130—132°/12 mm.
Unaffected by cold dilute hydrochloric acid.	Decomposed by cold dilute hydrochloric acid.
With dry ammonia, it yields the additive compound, $\text{CO}_2\text{Me}\cdot\text{C}(\text{OMe})(\text{NHPh})\cdot\text{NH}_2$ (m. p. 215°).	Unaffected by dry ammonia.

It will be noticed, further, that the properties of the silver oxide product are analogous to those of all the now numerous examples of aryl-substituted imino-ethers.

The action of the bases named at the commencement of this paper on methyl dichloro-oxalate was re-examined, and the results obtained were:

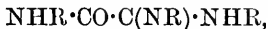
(1) Piperidine and phenylhydrazine behave in the manner described by Anschütz and Stiepel, yielding the ortho-diamide,



and the imino-compound,  $\text{CO}_2\text{Me}\cdot\text{C}(\text{N}\cdot\text{NHPh})\cdot\text{OMe}$ , respectively.

(2) With aniline and *p*-toluidine, there was no evidence of the formation of either diamido-compounds or imino-ethers.

With the latter bases, the main and apparently primary products of the condensation in the cold are arylamidino-oxalic esters of the type  $\text{CO}_2\text{Me}\cdot\text{C}(\text{NR})\cdot\text{NHR}$ , of which I have previously described the ethyl ester,  $\text{CO}_2\text{Et}\cdot\text{C}(\text{NPh})\cdot\text{NHPh}$  (Trans., *ibid.*, 699). Again, when the action occurs in warm xylene solution, the chief product is an amidino-ester, accompanied, however, by substituted oxamates and oxamides, and by substituted formamidines,  $\text{HC}(\text{NR})\cdot\text{NHR}$ , carbon dioxide, and methyl chloride, whilst amidinoamides,



are obtained in all the condensation processes. I am of opinion that the oxamates and oxamides are formed from the condensation of the arylamine with methyl oxalate, from which the dichloro-compound is separated only with difficulty. The formation of formamidine is explicable in the light of the transformations of the amidino-esters to be described later.

Anschütz and Stiepel have merely given the formation and boiling point and quoted the analyses of the dipiperidide. I find that this compound is very easily hydrolysed by water, this action leading, doubtless, in the first instance to the formation of methyl oxalate and

piperidine,  $\text{CO}_2\text{Me}\cdot\text{C}(\text{C}_5\text{NH}_{10})_2\cdot\text{O}\cdot\text{CH}_3 + \text{H}_2\text{O} = (\text{CO}_2\text{Me})_2 + 2\text{NH}\cdot\text{C}_5\text{H}_{10}$ , the ester being instantly hydrolysed, yielding methyl alcohol and piperidine oxalate. This behaviour is entirely in accordance with that observed by Willstätter (*Ber.*, 1902, 35, 1386) with methyl tetramethyldiaminomalonate, and by Conrad and Reinbach (*Ber.*, 1902, 35, 522) with methyl dianilinomalonate. It is therefore exceedingly probable that the diarylamido-compounds of Anschütz and Stiepel would undergo a similar change, but, nevertheless, the first step in their method for the separation of the supposed diamides consists in shaking the ethereal solution of the product of reaction with water slightly acidified with dilute hydrochloric acid. Moreover, Conrad and Brückner (*Ber.*, 1891, 24, 3003) have pointed out the ease with which diaminomalonamide passes by loss of ammonia into the imide,



The balance of evidence favours the view that a diamino-compound containing the group  $\text{CX}(\text{NHR})_2$  is an unstable substance, and readily loses either  $\text{NH}_2\text{R}$  or  $\text{HX}$ . In the reaction now under discussion, the

decomposition is of the second type, the diamide,  $\text{C}(\text{NHR})_2$   $\begin{array}{c} \text{NR}\cdot\text{H} \\ \text{OMe} \end{array}$ ,

supposing it actually to be the first product of reaction, parting with methyl alcohol and passing into the relatively stable amidine. I think the amidino-esters are formed in anhydrous ethereal solution at  $0^\circ$ , for the liquid instantly acquires the characteristic yellow colour of solutions of the amidino-ester when the base is added to the ethereal solution of dichloro-ester; moreover, supposing the ortho-amide to exist in the anhydrous solution, it would most probably be decomposed when water is added, as indicated above.

As regards the imino-compound derived from phenylhydrazine, which I propose to designate phenylaminoimino-oxalic dimethyl ether, it is monomolecular, and probably has the composition  $\text{CO}_2\text{Me}\cdot\text{C}(\text{NHPh})\cdot\text{OMe}$ . Its physical properties (it is a solid melting at  $123-125^\circ$ ) are unlike those of the imino-ethers containing one nitrogen atom, but as it is the only imino-compound of its type, we are at present without analogies to guide us in anticipating its probable properties. The corresponding acid,  $\text{CO}_2\text{H}\cdot\text{C}(\text{N}\cdot\text{NHPh})\cdot\text{OMe}$ , is very unstable; when boiled with dilute methyl alcohol, it yields carbon dioxide, oxalic acid, and formazan,  $\text{HC}(\text{N}\cdot\text{NHPh})\cdot\text{N}\cdot\text{NPh}$ .

I. *The Condensations of Piperidine and of Phenylhydrazine with Methyl Dichloro-oxalate.*

*Formation of Dipiperidido-oxalic Dimethyl Ether.*—Better results were obtained by employing light petroleum instead of dry ether as a diluent. The piperidine (34 grams) was added slowly to the cold solution of methyl dichloro-oxalate (30 grams) in 150 c.c. of light petroleum. After 4 days, the liquid was filtered and sufficient benzene added to ensure solution of the liquid product, which is insoluble in petroleum. On distillation in a partial vacuum, a yellow oil was collected, and a large, tarry residue remained; on fractionation, the distillate boiled between  $105^{\circ}$  and  $130^{\circ}/15$  mm., the main fraction (4 grams), however, distilling at  $106\text{--}109^{\circ}/15$  mm. Anschütz and Stiepel give the boiling point as  $166^{\circ}/20$  mm.

0.1103 gave 0.2510  $\text{CO}_2$  and 0.0961  $\text{H}_2\text{O}$ .  $\text{C} = 62.1$ ;  $\text{H} = 9.7$ .

0.1498 „ 13.7 c.c. moist nitrogen at  $14.5^{\circ}$  and 756 mm.  $\text{N} = 10.7$

$\text{C}_{14}\text{H}_{26}\text{O}_3\text{N}_2$  requires  $\text{C} = 62.2$ ;  $\text{H} = 9.6$ ;  $\text{N} = 10.4$  per cent.

The compound is readily dissolved by water, being thereby resolved, as mentioned in the introduction, into methyl alcohol and piperidine oxalate.

*Formation of Phenylaminoimino-oxalic Dimethyl Ether.*

When 43 grams of phenylhydrazine and 17 grams of methyl dichloro-oxalate are employed in 60—70 c.c. of cold ether, about 3 grams of Anschütz and Stiepel's compound are obtainable, the yields varying in different preparations. Oxalphenylhydrazide is also produced (probably from the methyl oxalate present in the chloro-ester), and was separated as a powder insoluble in the ordinary solvents, melting above  $280^{\circ}$ , and, after crystallisation from phenol and alcohol, giving  $\text{C} = 62.3$ ;  $\text{H} = 5.3$  per cent., instead of the calculated  $\text{C} = 62.2$ ;  $\text{H} = 5.2$ .

The imino-compound was not separated by Anschütz and Stiepel's method, but by washing the ethereal solution repeatedly with sodium acetate solution and then with water. After crystallisation from dilute methyl alcohol, it melted at  $123\text{--}124^{\circ}$ .

0.1812 gave 0.3826  $\text{CO}_2$  and 0.0954  $\text{H}_2\text{O}$ .  $\text{C} = 57.6$ ;  $\text{H} = 5.85$ .

0.1504 „ 17.2 c.c. moist nitrogen at  $13^{\circ}$  and 765 mm.  $\text{N} = 13.6$ .

$\text{C}_{10}\text{H}_{12}\text{O}_3\text{N}_2$  requires  $\text{C} = 57.7$ ;  $\text{H} = 5.8$ ;  $\text{N} = 13.5$  per cent.

0.3795 in benzene gave  $\Delta t = 0.41^{\circ}$ . M. W. = 198.

$\text{C}_{10}\text{H}_{12}\text{O}_3\text{N}_2$  requires M. W. = 208.

*Phenylaminoimino-oxalic acid methyl ether*,  $\text{CO}_2\text{H}\cdot\text{C}(\text{N}\cdot\text{NHPh})\cdot\text{OMe}$ , resulted when equivalent proportions of the ester and very concentrated potassium hydroxide were shaken together, the hydrolysis being completed by adding finally a little alcohol and gently warming. The mixture was then diluted and, after filtration, acidified with cold dilute hydrochloric acid under a layer of ether. The solvent was driven off in a current of air and the acid brought into solution by very gently warming it for a few moments with methyl alcohol, when, on adding water, nearly colourless leaflets separated, which decomposed vigorously at  $99-100^\circ$ .

0.1396 gave 0.2848  $\text{CO}_2$  and 0.0680  $\text{H}_2\text{O}$ .  $\text{C} = 55.6$ ;  $\text{H} = 5.4$ .

$\text{C}_9\text{H}_{10}\text{O}_3\text{N}_2$  requires  $\text{C} = 55.7$ ;  $\text{H} = 5.1$  per cent.

When boiled with dilute methyl alcohol, the acid rapidly decomposed, carbon dioxide being evolved, whilst the liquid acquired a dark blood-red colour. On adding water, dark red needles separated, which, after crystallisation from dilute methyl alcohol and drying over sulphuric acid, decomposed at  $115-117^\circ$ , and gave, with sulphuric acid, the deep blue coloration changing to red on dilution, which is characteristic of formazan,  $\text{HC}(\text{N}\cdot\text{NHPh})\cdot\text{N}\cdot\text{NPh}$ .

0.1274 gave 0.3255  $\text{CO}_2$  and 0.0638  $\text{H}_2\text{O}$ .  $\text{C} = 69.7$ ;  $\text{H} = 5.6$ .

0.0820 „ 16.9 c.c. moist nitrogen at  $11^\circ$  and 762 mm.  $\text{N} = 24.6$ .

$\text{C}_{13}\text{H}_{12}\text{N}_4$  requires  $\text{C} = 69.6$ ;  $\text{H} = 5.35$ ;  $\text{N} = 25.0$  per cent.

## II. *Semi-N-arylimino-oxalic Ethers.*

*Semi-N-phenylimino-oxalic Dimethyl Ether*,  $\text{CO}_2\text{Me}\cdot\text{C}(\text{NPh})\cdot\text{OMe}$ .—This compound results from the methylation of methyl oxanilate with dry silver oxide and methyl iodide, along with the isomeric methyl phenylmethyloxamate,  $\text{CO}_2\text{Me}\cdot\text{CO}\cdot\text{NMePh}$  (compare Trans., *ibid.*). The reaction was carried out in the manner previously described, some benzene being added to ensure the solution of the oxanilate, and the mixture being gently boiled during 3 hours. The liquid mixture of isomeric methyl compounds was separated by fractionation in a partial vacuum, and by taking advantage of the fact that the imino-ether dissolves in light petroleum, the substituted oxamate being insoluble in that liquid. From 36 grams of methyl oxanilate, 7 grams of imino-ether boiling at  $130-132^\circ/12$  mm., and 4 grams of the isomeride boiling at  $170-175^\circ/13$  mm. were obtained.

The imino-ether was analysed:

0.1495 gave 0.3390  $\text{CO}_2$  and 0.0800  $\text{H}_2\text{O}$ .  $\text{C} = 61.8$ ;  $\text{H} = 5.9$ .

0.2513 „ 16.2 c.c. moist nitrogen at  $16^\circ$  and 757 mm.  $\text{N} = 7.5$ .

$\text{C}_{10}\text{H}_{11}\text{O}_3\text{N}$  requires  $\text{C} = 62.2$ ;  $\text{H} = 5.7$ ;  $\text{N} = 7.2$  per cent.

The imino-ether forms a slightly yellow, fairly mobile liquid soluble in petroleum and other organic solvents. It is dissolved on shaking with cold dilute hydrochloric acid, undergoing the ordinary imino-ether hydrolysis, whilst anhydrous hydrogen chloride produces a sticky hydrochloride. A comparison of its properties with those of Anschütz and Stiepel's compound has been already made in the introduction.

*Methyl phenylmethyloxamate* is a viscid, yellow liquid insoluble in dilute acids and in light petroleum. On hydrolysis with cold alcoholic potassium hydroxide, it yields Guareschi's methyloxanilic acid, which, after drying, melts at  $122^{\circ}$ . The ester was analysed with the following result:

0.1945 gave 12.3 c.c. moist nitrogen at  $15.5^{\circ}$  and 765 mm.  $N = 7.4$ .

$C_{10}H_{11}O_3N$  requires  $N = 7.2$  per cent.

*Semi-N-p-tolylimino-oxalic Diethyl Ether*,  $CO_2Et \cdot C(N \cdot C_7H_7) \cdot OEt$ .—This imino-ether was easily obtained by the silver oxide ethylation of ethyl *p*-tolyloxamate, 20 grams of which gave 17 grams of crude imino-ether, yielding on fractionation 10 grams boiling at  $160\text{--}162^{\circ}/14\text{--}15$  mm.

0.1456 gave 0.3546  $CO_2$  and 0.0950  $H_2O$ .  $C = 66.4$ ;  $H = 7.2$ .

$C_{13}H_{17}O_3N$  requires  $C = 66.4$ ;  $H = 7.2$  per cent.

The compound possesses the characteristics of its congeners; its condensation with *p*-toluidine is described in the next section.

*The ethylation of the substituted methyloxamates by means of silver oxide.*—This reaction presented an interesting case of the interchange of alkyls in the carboxylic ester group during the alkylation of the  $CO \cdot NH$  residue, comparable results being obtained with methyl oxanilate and methyl *p*-tolyloxamate. A description of the ethylation of methyl oxanilate will therefore suffice.

On effecting the ethylation in the usual way, the liquid imino-ether did not show any constant boiling point but distilled between  $140^{\circ}$  and  $152^{\circ}/13\text{--}14$  mm. There was no difference in composition, discernible by analysis, between the extreme fractions; the lowest fraction gave  $C = 64.7$ ;  $H = 6.7$ ; the highest  $C = 64.7$ ;  $H = 6.8$  per cent.

$CO_2Me \cdot C(NPh) \cdot OEt$  requires  $C = 63.8$ ;  $H = 6.3$ .

$CO_2Et \cdot C(NPh) \cdot OEt$  requires  $C = 65.15$ ;  $H = 6.8$  per cent.

A further treatment of the product made no difference in the composition; the interchange therefore occurred during alkylation. That ethyl imino- and not methyl imino-ether was formed is probable, for no less volatile *N*-alkylated esters were detected, and on condensation with aniline a mixed amidino-ester resulted.

*Action of Dry Ammonia on the Imino-ethers.*

In order to test the additive reaction in the sense of the scheme,  $\text{CO}_2\text{Me}\cdot\text{C}(\text{NR})\cdot\text{OMe} + \text{NH}_3 = \text{CO}_2\text{Me}\cdot\text{C}(\text{NH}_2)(\text{NHR})\cdot\text{OMe}$ , described by Anschütz and Stiepel, and which they suppose to be general, the action of ammonia was examined in cold ethereal solutions of the oxalimino-ethers.

Dry ammonia was passed into cooled solutions of the semi-*N*-phenylimino-oxalic dimethyl and diethyl ethers, and of semi-*N-p*-tolylimino-oxalic diethyl ether in absolute ether. After 24 hours, no solid had separated, and the unaltered imino-ethers were recovered, having precisely the same properties as before treatment.

The action of dry ammonia under like conditions was also studied with benziminoethyl ether, *N*-phenyl- and *N-o*-tolyl-acetiminoethyl ethers, *N*-benzylbenziminoethyl ether, *N-o*-tolylbenziminoethyl ether, and *N*-phenylbenziminomethyl, ethyl, and propyl ethers. No action occurred with any of these compounds, nor was the formation of amidines noticed under comparable experimental conditions.

*Hydrolysis of the N-Aryloxalimino-ethers.*—All these imino-ethers can be hydrolysed by concentrated potassium hydroxide with the formation of the potassium salts of the imino-ether acids,  $\text{CO}_2\text{K}\cdot\text{C}(\text{NR})\cdot\text{OR}'$ . The case of semi-*N*-phenylimino-oxalic diethyl ether is typical. When shaken with concentrated potassium hydroxide, a solid potassium salt, insoluble in alcohol, separated, which, however, was not obtained sufficiently pure for analysis. On acidifying the aqueous solution of the salt with dilute hydrochloric acid, each drop of acid caused the momentary formation of an oily liquid (almost certainly the free imino-ether acid), which rapidly disappeared, and the solution finally contained only oxalic acid, aniline hydrochloride, and alcohol. The free acids thus undergo the hydrolytic hydrolysis far more readily than do the corresponding esters.

### III. *Formation of Arylamidino-oxalic Esters. Reaction between Methyl Dichloro-oxalate and Aniline or p-Toluidine.*

*Arylamidino-oxalic Esters from the Imino-ethers.*—As previously stated (Trans., *ibid.*, 699), semi-*N*-phenylimino-oxalic diethyl ether with one molecule of aniline at 100° easily yields the corresponding amidino-ester (m. p. 73—74°). This method of formation is not suitable for the preparation of the analogous methyl ester, partly owing to the difficulty of crystallising that compound, and to the comparative ease with which it is decomposed by heat, but mainly to the diffi-

culty of preparing large quantities of the imino-ether by the silver oxide method. The production of the methyl ester from an ethyl-imino-methyl ester failed owing to the interchange of alkyls in the carboxylic ester group already described, the product obtained from the mixed ether being a mixture of methyl and ethyl amidino-esters melting at 65—70° (the melting points of the ethyl and methyl esters being 73—74° and 65—66° respectively).

*Methyl diphenylamidino-oxalate* was easily prepared from the ethyl ester, and therefore from the diethylimino-ether, by allowing the solution of the ethyl ester in methyl alcohol containing a trace of sodium methoxide to remain in the cold for 2 or 3 days (compare Purdie, Trans., 1887, 51, 627). On adding water to the solution, which now contained the pure methyl ester, that compound separated in aggregates of pale yellow needles which, after recrystallisation from methyl alcohol and water, melted constantly at 65—66°.

The ester, which was first obtained pure by this method, subsequently served as a nucleus for the crystallisation of the crude product of Anschütz and Stiepel's reaction.

*Ethyl di-p-tolylamidino-oxalate*,  $\text{CO}_2\text{Et} \cdot \text{C}(\text{NC}_7\text{H}_7) \cdot \text{NH} \cdot \text{C}_7\text{H}_7$ , produced by warming the diethylimino-ether and a molecular proportion of *p*-toluidine at 100° for 2 or 3 hours, crystallised in colourless needles from dilute alcohol and melted at 98—100°.

0.1450 gave 0.3880  $\text{CO}_2$  and 0.0900  $\text{H}_2\text{O}$ .  $\text{C} = 73.0$ ;  $\text{H} = 6.9$ .

$\text{C}_{18}\text{H}_{20}\text{O}_2\text{N}_2$  requires  $\text{C} = 73.0$ ;  $\text{H} = 6.7$  per cent.

The platinichloride separated from dilute hydrochloric acid solution in yellow needles decomposing at 115—120°.

0.2500 gave 0.0476 Pt.  $\text{Pt} = 19.0$ .

$(\text{C}_{18}\text{H}_{20}\text{O}_2\text{N}_2)_2 \cdot \text{H}_2\text{PtCl}_6$  requires  $\text{Pt} = 19.4$  per cent.

When the solution of ethyl ester in methyl alcohol with a trace of sodium methoxide remained in the cold during several days, the methyl ester (see above) was produced, and formed colourless needles melting at 103.5—104.5°.

*Aniline and Methyl Dichloro-oxalate in the Cold.*—The reaction was carried out as described by Anschütz and Stiepel. The hydrochloride of the organic base was precipitated at 0° from ethereal solution by means of hydrogen chloride dissolved in the same solvent, as a colourless solid forming needles decomposing at 92—95°. Anschütz and Stiepel give no melting or decomposing point for the hydrochloride or the platinichloride of their diamido-base. They state that their hydrochloride, on exposure or on heating, easily parts with hydrogen chloride, regenerating the original base. The hydrochloride of methyl diphenylamidino-oxalate is exceedingly hygroscopic, rapidly

liquefying to a yellow solution when exposed to air; the nature of the decomposition which occurs on heating is explained in the next section.

After liberation of the base from the cold solution of the hydrochloride by sodium carbonate, desiccation of the ethereal extract with calcium chloride, and evaporation in a vacuum, Anschütz and Stiepel obtained the substance in a solid form, and quote analyses, the results of which agree neither with the composition of a dianilido-compound nor with that of the amidino-ester. Unfortunately, they do not state what is the melting point of their solid base. The constitution assigned to it and its *p*-tolyl analogue is deduced by these authors from chlorine determinations in the hydrochlorides and full analysis of the platinichlorides. It seemed in every way preferable to secure pure solid specimens of the base, which were produced by means of nuclei of the pure base obtained as described in the preceding section. The product was therefore crystallised repeatedly from dilute methyl alcohol in ice-cold solution, when it melted constantly at 65–66°, and did not alter the melting point of a sample of the ester prepared from the corresponding ethyl compound. Moreover, the solid product gave rise to the same hydrochloride (decomposing at 92–95°) as that procured from the original product of reaction.

As methyl dichloro-oxalate has the characteristics of an acid chloride, it seemed likely that the condensation with the arylamines could be effected by the Schotten-Baumann method. As a matter of fact, the diphenyl amidino-ester was readily obtained in this way by employing sodium carbonate instead of sodium hydroxide and by taking about 1½ times the calculated amount of dichloro-ester. By the aid of a nucleus of pure product, the compound could be obtained crystalline after extracting the ethereal solution with hydrochloric acid, in order to separate the diphenylamidino-oxalanilide always produced in the condensations, and then reprecipitating with sodium carbonate, extracting with ether, evaporating the ethereal extract, and crystallising the product from cold dilute methyl alcohol.

Specimens of the methyl diphenylamidino-oxalate were analysed:

* 0.1430	gave 0.3710 CO <sub>2</sub> and 0.0727 H <sub>2</sub> O.	C = 70.75; H = 5.6.
* 0.1250	„ 11.8 c.c. moist nitrogen at 14° and 744 mm.	N = 10.8.
† 0.1670	„ 0.4340 CO <sub>2</sub> and 0.0856 H <sub>2</sub> O.	C = 70.9; H = 5.7.
‡ 0.1370	„ 0.3567 CO <sub>2</sub> „ 0.0689 H <sub>2</sub> O.	C = 71.0; H = 5.6.
‡ 0.1455	„ 14 c.c. moist nitrogen at 11° and 742 mm.	N = 11.2.
* 0.3030	„ 0.2750 AgI. OCH <sub>3</sub> = 12.0.	
C <sub>15</sub> H <sub>14</sub> O <sub>2</sub> N <sub>2</sub> requires C = 70.9; H = 5.5; N = 11.0; OCH <sub>3</sub> = 12.2		
per cent.		

\* From aniline and methyl dichloro-oxalate.

† By the modified Schotten-Baumann method.

‡ From the ethyl ester.

The platinichloride, prepared either according to Anschütz and Stiepel's method or by dissolving the free base in cold concentrated hydrochloric acid and adding platinic chloride, formed yellow crystals which decomposed at  $198^{\circ}$ .

0.3800 gave 0.0820 Pt.  $Pt = 21.6$ .

$(C_{15}H_{14}O_2N_2)_2H_2PtCl_6$  requires  $Pt = 21.2$  per cent.

*Aniline and Methyl Dichloro-oxalate in Warm Xylene Solution.*—

Very small amounts of the by-products mentioned in the introduction were obtained along with the methyl diphenylamidino-oxalate on using Anschütz and Stiepel's method, which consists in adding aniline to the solution of dichloro-ester in xylene on the boiling water-bath. Larger quantities were produced when the xylene solution was first warmed at  $130^{\circ}$  in an oil-bath. In that case, an evolution of gas and white fumes was noticed, and carbon dioxide and methyl chloride were detected. After separating aniline hydrochloride by means of water and a little hydrochloric acid, methyl diphenylamido-oxalate was extracted with dilute hydrochloric acid, leaving a xylene solution of the neutral products and a considerable amount of solid; the latter, when agitated with ammonia solution and ether, yielded oxanilide, whilst diphenylformamidine (m. p.  $133^{\circ}$ ) passed into the ethereal solution and was subsequently crystallised from dilute alcohol. The xylene solution deposited methyl oxanilate together with small quantities of oxanilide and diphenylamido-oxanilide. Three grams of the oxanilate were obtained from 42 grams of aniline and 25 grams of dichloro-ester. Unless the product is repeatedly crystallised, the presence of small quantities of oxanilide along with the methyl oxanilate (m. p.  $111-112^{\circ}$ ) may, on analysis, lead to a percentage of carbon as high as that required for the methylimino-ether. Thus, after one crystallisation from alcohol, the analysis gave  $C = 62.2$ ;  $H = 5.2$ ; after recrystallisation from benzene and light petroleum, the numbers were  $C = 60.9$ ;  $H = 5.2$ , and after two further crystallisations from benzene the following results were obtained:  $C = 60.5$ ,  $60.5$ ;  $H = 5.2$ ,  $5.1$ ;  $N = 7.85$ . Methyl oxanilate,  $C_9H_9O_3N$ , and the methylimino-ester,  $C_{10}H_{11}O_3N$ , require  $C = 60.3$ ;  $H = 5.0$ ;  $N = 7.8$ , and  $C = 62.2$ ;  $H = 5.7$ ;  $N = 7.2$  respectively.

The melting point of the substance remained constant at  $111-112^{\circ}$ , and no alteration of the melting point of pure methyl oxanilate was noticed on mixing the two specimens.

As is well known, the action of ammonia on the oxanilic esters produces phenyloxamide, melting, after crystallisation from acetone, at  $226-227^{\circ}$ , and, in this connection, attention may be drawn to the circumstance that the following melting points of the four compounds, to which Anschütz and Stiepel assign the following constitutions:

$\text{CO}_2\text{Me}\cdot\text{C}(\text{NPh})\cdot\text{OMe}$  (m. p.  $111^\circ$ );  $\text{CO}_2\text{Me}\cdot\text{C}(\text{NH}_2)(\text{NHPh})\cdot\text{OMe}$  (m. p.  $215^\circ$ );  $\text{CO}_2\text{Me}\cdot\text{C}(\text{N}\cdot\text{C}_7\text{H}_7)\cdot\text{OMe}$  (m. p.  $145^\circ$ );

$\text{CO}_2\text{Me}\cdot\text{C}(\text{NH}_2)(\text{NHC}_7\text{H}_7)\cdot\text{OMe}$  (m. p.  $236^\circ$ );

are either identical or very nearly so with those of the substituted oxamates and oxamides :

$\text{CO}_2\text{Me}\cdot\text{CO}\cdot\text{NHPh}$  ( $111-112^\circ$ );  $\text{NH}_2\cdot\text{CO}\cdot\text{CO}\cdot\text{NHPh}$  (m. p.  $226-227^\circ$ );

$\text{CO}_2\text{Me}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_7\text{H}_7$  ( $145^\circ$ );  $\text{NH}_2\cdot\text{CO}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_7\text{H}_7$  (m. p.  $226^\circ$ ).

*p-Toluidine and Methyl Dichloro-oxalate in the Cold.*

The condensation was effected either in the manner described by Anschütz and Stiepel, or by means of the modified Schotten-Baumann process (see p. 992).

Anschütz and Stiepel mention that the ethereal solution of the product on evaporation leaves a solid mass, which, on crystallisation from ether, forms fine, white, feathery crystals melting at  $105^\circ$ , but state that they did not get the substance in a state of purity owing to its ready solubility in all neutral solvents. As a matter of fact, the product, which may be most easily crystallised by adding water to the solution in alcohol, after several crystallisations forms fine, colourless crystals melting at  $103^\circ$ , so that it is exceedingly likely that the compound, which I formulate as methyl di-*p*-tolylamidino-oxalate, is actually the same substance as that procured by Anschütz and Stiepel, to which they assigned the constitution of a di-*p*-toluido-ester, from evidence based on the analysis of the hydrochloride and platinichloride, the decomposing points of which salts they did not, however, indicate. Samples of the methyl di-*p*-tolylamidino-oxalate were analysed.

\* 0.1520 gave 0.4029  $\text{CO}_2$  and 0.0891  $\text{H}_2\text{O}$ .  $\text{C}=72.3$ ;  $\text{H}=6.5$ .

† 0.1530 „ 0.4061  $\text{CO}_2$  „ 0.0896  $\text{H}_2\text{O}$ .  $\text{C}=72.4$ ;  $\text{H}=6.5$ .

\* 0.1240 „ 10.8 c.c. moist nitrogen at  $17^\circ$  and 760 mm.  $\text{N}=10.1$ .

\* 0.3095 „ 0.2538 AgI.  $\text{OCH}_3=10.8$ .

$\text{C}_{17}\text{H}_{18}\text{O}_2\text{N}_2$  requires  $\text{C}=72.3$ ;  $\text{H}=6.4$ ;  $\text{N}=9.9$ ;  $\text{OCH}_3=11.0$  per cent.

The hydrochloride of methyl di-*p*-tolylamidino-oxalate, which forms colourless needles, decomposing between  $100^\circ$  and  $105^\circ$ , is hygroscopic like the phenyl compound.

The platinichloride formed yellow crystals decomposing at  $172^\circ$ .

0.5106 gave 0.1028 Pt.  $\text{Pt}=20.1$ .

$(\text{C}_{17}\text{H}_{18}\text{O}_2\text{N}_2)_2\text{H}_2\text{PtCl}_6$  requires  $\text{Pt}=20.0$  per cent.

\* From *p*-toluidine and methyl dichloro-oxalate.

† From the ethyl ester.

*p*-Toluidine and Methyl Dichloro-oxalate in Warm Xylene Solution.—The course of the reaction and the method of separation of the products were precisely similar to those already given in the case of the aniline condensation. In addition to methyl di-*p*-tolylamidino-oxalate, small quantities of di-*p*-tolylamidino-oxalotoluidide (m. p. 182°), di-*p*-tolylformamidine, di-*p*-tolylloxanilide, and methyl *p*-tolylloxamate (m. p. 145°) were obtained. The oxamate was carefully purified by several crystallisations from alcohol.

This ester, which can be readily prepared by boiling together molecular proportions of methyl oxalate and *p*-toluidine, has not been previously described.

0.1335 gave 0.3100 CO<sub>2</sub> and 0.0716 H<sub>2</sub>O. C = 62.4; H = 5.9.

0.1786 „ 11.5 c.c. moist nitrogen at 15° and 767.7 mm. N = 7.6.  
CO<sub>2</sub>Me·CO·NHC<sub>7</sub>H<sub>7</sub> requires C = 62.2; H = 5.7; N = 7.25 per cent.

#### IV. Transformations of the Arylamidino-oxalic Esters.

*Formation of the Amidino-oxalic Acids and of Substituted Formamidines.*—When the arylamidino-oxalic esters are hydrolysed by means of cold alcoholic potassium hydroxide, the potassium salts of the corresponding amidino-acids result, and on acidification the acids themselves are precipitated as microcrystalline, yellow solids. Hydrolysis also occurs when the solutions of the esters in dilute hydrochloric acid are left for a few days in the cold, when the acids are gradually deposited as long needles.

Neither the diphenyl- nor the di-*p*-tolyl-amidino-oxalic acid has a definite melting point; when quickly heated, these compounds fuse and evolve carbon dioxide at about 100°, quickly resolidify, and then melt again between 130° and 140°; on warming slowly, they sinter at about 100°. When dissolved in hot alcohol, the crystals which separate are those of diphenyl- and di-*p*-tolyl-formamidines respectively.

The diphenylamidino-oxalic acid was analysed with the following result:

0.1426 gave 0.3655 CO<sub>2</sub> and 0.0669 H<sub>2</sub>O. C = 69.9; H = 5.2.

0.1105 „ 10.9 c.c. moist nitrogen at 16° and 768 mm. N = 11.6.  
CO<sub>2</sub>H·C(N·C<sub>6</sub>H<sub>5</sub>)·NH·C<sub>6</sub>H<sub>5</sub> requires C = 70.0; H = 5.0; N = 11.7 per cent.

The di-*p*-tolyl homologue was also analysed:

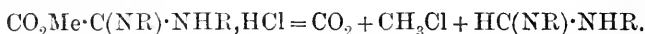
0.1530 gave 0.4024 CO<sub>2</sub> and 0.0846 H<sub>2</sub>O. C = 71.7; H = 6.1.

C<sub>16</sub>H<sub>16</sub>O<sub>2</sub>N<sub>2</sub> requires C = 71.7; H = 6.0 per cent.

The bases produced by the elimination of carbon dioxide on heating

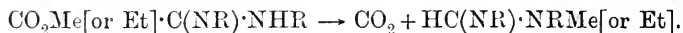
were shown by analysis and a study of their properties to be identical with the substituted formamidines.

The substituted formamidines may also be obtained from the amidino-oxalic series by heating the hydrochlorides of the esters. Thus, when the hydrochloride of methyl diphenylamidino-oxalate was warmed at 100—110°, methyl chloride and carbon dioxide were evolved, and the residual mass consisted mainly of diphenylformamidine and a little oxanilide:



*Effect of Heating the Arylamidino-oxalic Esters.*

Anschütz and Stiepel state that their dianilido-base decomposes at 170° under diminished pressure, giving rise to an isonitrile. When the arylamidino-oxalic esters are heated in a tube, carbon dioxide is evolved and an odour of isonitrile is perceived; the main reaction being the production of alkylated formamidines,



The reaction was carried out in detail with methyl di-*p*-tolylamidino-oxalate; decomposition commenced at 220°/70 mm., and was pronounced at 260°. When the evolution of gas had ceased, about one-half of the dark-coloured residue distilled over at 228°/17 mm., and after two crystallisations from dilute methyl alcohol yielded slender, colourless needles of a base which melted at 68—69°.

0.1382 gave 0.4090 CO<sub>2</sub> and 0.0968 H<sub>2</sub>O. C = 80.7; H = 7.8.

0.1434 „ 14.5 c.c. moist nitrogen at 18° and 757.5 mm. N = 11.6.

These numbers correspond best with those calculated for di-*p*-tolylmethylformamidine, C<sub>16</sub>H<sub>18</sub>N<sub>2</sub>, which requires C = 80.6; H = 7.6; N = 11.8 per cent.

This amidine may also be prepared by methylating di-*p*-tolylformamidine with methyl iodide, a sample thus prepared being identical with that described above.

*Methylation of Methyl Di-p-tolylamidino-oxalate.*—Five grams of ester and 15 grams of methyl iodide were boiled together for three hours, and then left for twelve hours, when an oily iodide and a small amount of solid iodide (that of di-*p*-tolylformamidine) were produced, the liquid compound being separable from the solid by means of ether. The base obtained from the liquid salt fused at 91—92° after three crystallisations from dilute alcohol, and resembled the present amidine.

0.1230 gave 0.3300 CO<sub>2</sub> and 0.0800 H<sub>2</sub>O. C = 73.2; H = 7.2.

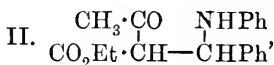
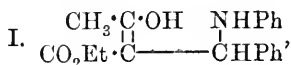
CO<sub>2</sub>Me·C(N·C<sub>7</sub>H<sub>7</sub>)·NMe·C<sub>7</sub>H<sub>7</sub> requires C = 73.0; H = 6.75 per cent,



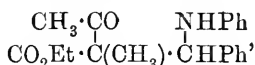
CI.—*The Additive Products of Benzylideneaniline with Ethyl Acetoacetate and Ethyl Methylacetoacetate.*

By FRANCIS ERNEST FRANCIS and MILLICENT TAYLOR.

SCHIFF'S explanation of the constitution of the additive products formed when ethyl acetoacetate and benzylideneaniline interact, agrees fairly well with the known facts. He considered that one was the "enol," and the other the "keto" form of ethyl benzylideneaniline-acetoacetate:



but there is not yet sufficient evidence to show which isomeride corresponds with either of these formulæ. Schiff's views as to the nature of the disturbance brought about by the catalytic reagents, sodium ethoxide, and piperidine, although probably incorrect, led him to assign the first formula to the less fusible isomeride, and the second to the more fusible compound. When the existence of two forms becomes impossible, as in the case of the additive product of benzylideneaniline and ethyl methylacetoacetate,



it should be possible to purify the substance with less difficulty than in previous cases so that a compound with constant melting point would be obtained, the peculiar behaviour of the catalytic reagents having disappeared. This we have found to be the case, although the substance is much more difficult to obtain than the corresponding compound from ethyl acetoacetate; it is easily purified, exists in one form, and the catalytic reagents employed in other cases had no effect. This corroborates the views put forward as to the nature of the additive products, and renders it quite probable that at least two isomerides should exist in the case of ethyl acetoacetate, thus supporting the work of previous investigators.

Morrell and Bellars (Trans., 1903, 83, 1292), however, consider that they have shown that the compound obtained from benzylideneaniline and ethyl acetoacetate only exists in one form, namely, that melting between 78° and 80°. This result is somewhat surprising in view of the large amount of work which has been done on this subject, all pointing to the existence either of at least two modifications or of the impossibility of separating the constituents of the

mixtures of isomeric derivatives (R. Schiff, *Ber.*, 1898, 31, 205, 601; P. Rabe, *Ber.*, 1902, 35, 3947; F. E. Francis, *Ber.*, 1903, 36, 937; M. Taylor, *Ber.*, 1903, 36, 941). The method relied on by Morrell and Bellars, and from which their deduction is drawn, consists in the use of pure benzene as solvent; this must be considered as being untrustworthy, especially as no analyses are given of the less fusible preparations.

We found that in the absence of traces of piperidine, the crude additive product had its melting point raised to that of the less fusible isomeride merely by washing with a solvent, but when this catalytic reagent was employed then the melting point of the original substance could not be similarly raised.

Further, Morrell and Bellars' suggestion that the less fusible substance was contaminated with benzylidenediaceoacetate is most improbable, since this substance contains no nitrogen and 7.8 per cent. less carbon than the additive product, and consequently could not possibly have escaped detection.

Since only one form of the additive product of ethyl methylacetoacetate and benzylideneaniline could be isolated, and as this substance must have the ketonic group, according to the generally accepted view of the constitution of such derivatives, it is probable that the less fusible modifications obtained from both methyl and ethyl acetoacetates have also the corresponding ketonic configuration. As regards the more fusible forms, it is unlikely, from what is known of the action of the so-called catalytic reagents, that piperidine should completely change one isomeride into the other, as Schiff suggested. It is more probable that such a reagent would rapidly bring about equilibrium between the two dynamic isomerides, and that the substances obtained through its agency are mixtures of ketonic and enolic forms of the additive products, the latter probably predominating. This would account for the difficulty experienced in obtaining a substance with a constant melting point when piperidine is employed, but even in its absence a certain quantity of the mixture appears to be present, and it is only when this is dissolved out that the less fusible modifications, the ketonic isomerides, are isolated.

#### EXPERIMENTAL.

Molecular quantities of benzylideneaniline and ethyl methylacetoacetate were mixed and left for five weeks under the following conditions:

(a) Without addition of sodium ethoxide and piperidine, (b) with traces of piperidine, (c) with traces of sodium ethoxide.

At the end of this time only partial crystallisation had taken place

in each case. After repeatedly washing the crude products, first with light petroleum and finally with benzene, a white substance melting at  $123^{\circ}$  was obtained from the three preparations, the melting point of which remained constant on repeated crystallisation. As in the case of the previously described additive products, the melting point depended on the initial temperature employed in the determination, and to obtain uniformity, the substance was always put into the bath about  $5^{\circ}$  below its melting point as indicated by a preliminary observation.

The substance melting at  $123^{\circ}$  was left for 2 days in a benzene solution containing several drops of piperidine, but at the end of that period it crystallised with unchanged melting point on the addition of light petroleum.

When dissolved in benzene or ether, the compound gave no coloration with an ethereal solution of ferric chloride, although, when alcohol was used as solvent, the bluish-violet coloration of the free ester gradually appeared, the development of the colour being accelerated by warming.

(1)  $C = 74.04$ ;  $H = 7.12$ ;  $N = 4.42$ .

(2)  $C = 73.64$ ;  $H = 7.39$ ;  $N = 4.47$ .

$C_{20}H_{23}O_3N$  requires  $C = 73.85$ ;  $H = 7.08$ ;  $N = 4.31$  per cent.

The molecular weight was determined by the depression of the freezing point of nitrobenzene and benzene.

(1) 0.499 substance dissolved in 19.165 nitrobenzene:

Time.	20 minutes.	3½ hours.	4 hours.	5½ hours.
$\Delta t$ .....	$0.56^{\circ}$	$0.565^{\circ}$	$0.57^{\circ}$	$0.578^{\circ}$
M. W. ....	314	312	309	305

(2) 0.7158 substance dissolved in 13.444 benzene:

Time.	15 minutes.	3½ hours.	4 hours.
$\Delta t$ .....	$0.84^{\circ}$	$0.835^{\circ}$	$0.84^{\circ}$
M. W. ....	311	312	311

$C_{20}H_{23}O_3N$  requires M. W. = 325.

The molecular weight does not fall as rapidly in solution as does that of either ethyl or methyl benzylideneanilineacetoacetate; moreover, the substance crystallises well, shows little signs of decomposition, and the crystals themselves when carefully examined were all of the same form.

The formation of a hydrochloride was further evidence of the greater stability of this additive substance, for, when dissolved in cold benzene and treated successively with dry hydrogen chloride and light petroleum, it furnished white crystals, which, after rapidly washing

with the latter solvent and carefully drying under diminished pressure melted at  $61^{\circ}$ . On exposure to air these crystals rapidly decomposed, yielding among other products benzaldehyde and aniline hydrochloride.

An analysis made, after drying for 10 minutes, gave  $\text{Cl} = 9.85$ ,  $\text{C}_{20}\text{H}_{23}\text{O}_3\text{N}, \text{HCl}$  requires  $\text{Cl} = 9.82$  per cent.

This salt is immediately dissociated by water, giving the original additive product melting at  $123^{\circ}$ .

The above results clearly indicate that benzylideneaniline and ethyl methylacetoacetate yield only one additive product, which, however, is formed much more slowly than the additive products of either methyl or ethyl acetoacetate, and, unlike them, is more stable and gives rise to an unstable hydrochloride.

Similar attempts made to prepare the additive product of benzylideneaniline and ethyl or benzyl ethylacetoacetate were unsuccessful, the solutions, after 7 months, showing no signs of crystallisation.

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## CII.—*Notes on Analytical Chemistry.*

By GILBERT THOMAS MORGAN.

### I. *Separation of Arsenic by Distillation in Hydrogen Chloride.*

ARSENIC may be readily separated from antimony by the distillation method described by Piloty and Stock (*Ber.*, 1897, 30, 1649), which involves the heating, in a current of hydrogen chloride and hydrogen sulphide, of a mixture of an arsenate and an antimony salt dissolved in concentrated hydrochloric acid, the distillate when passed into cold water yielding arsenious sulphide.

When, however, the arsenic is present in the tervalent condition, the hydrogen sulphide need not be passed through the distilling flask, but only through the water contained in the receiver.

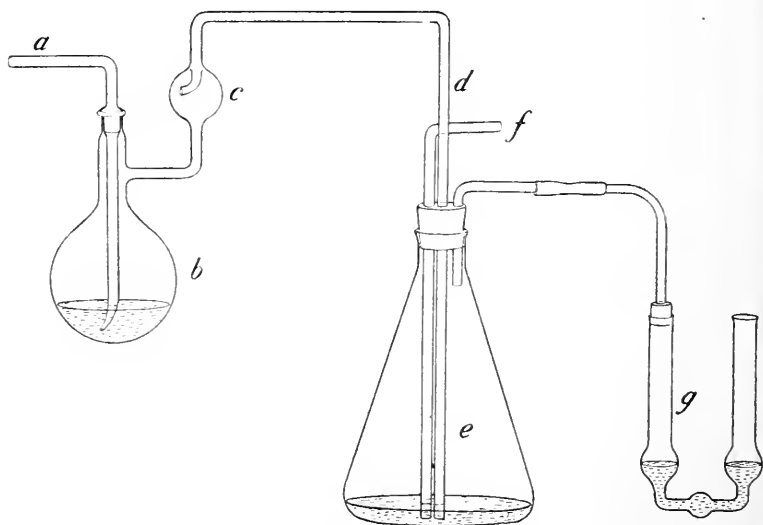
The modified apparatus indicated in the figure (p. 1002) is employed in operating on the mixed sulphides of arsenic and antimony obtained in the analysis of complex minerals.

The mixture of sulphides (0.2—0.5 gram) is suspended in 70—100 c.c. of concentrated hydrochloric acid contained in the flask *b* (capacity 300 c.c.) and distilled in a rapid current of hydrogen chloride, the distillate being received in about 250—350 c.c. of cold water saturated

with hydrogen sulphide (introduced through the tube *f*) and cooled by surrounding the flask *e* (capacity 700 c.c.) with ice.

The inlet tube, *a*, forms a part of the ground glass stopper of the distilling flask, and in this way any contact of the arsenious chloride vapour with organic matter is obviated. The arsenic is completely precipitated in the flask *e*, for in a successful experiment the water in the U-tube *g* remains clear throughout the operation.

The distillation of 0.5 gram of arsenious sulphide is completed within 40 minutes, but a rapid current of hydrogen chloride must be maintained; this, however, can be done with safety, as the introduction of the Kjeldahl bulb, *c*, greatly diminishes any risk of the antimony trichloride being carried over mechanically.



Experiments made on pure arsenious oxide showed that under these conditions the precipitated arsenious sulphide was tolerably free from uncombined sulphur, for when collected and weighed in a tared Gooch crucible after washing successively with alcohol, ether, carbon disulphide, and ether, and drying at 100°, the weight obtained approximated closely to the amount calculated for pure  $\text{As}_2\text{S}_3$ .

Satisfactory results were obtained with arseniferous minerals, such as tetrahedrite, by distilling weighed quantities (1–2 grams) in a current of chlorine, collecting the mixed volatile chlorides in hydrochloric acid containing tartaric acid (Thorpe, *Quantitative Analysis*, ed. 1891, p. 277) and distilling in the foregoing apparatus the sulphides obtained by precipitation from the acid solution. The antimony and

arsenic were in the first place weighed as trisulphides, the purity of the products being checked by estimating the antimony as tetroxide and the arsenic either as magnesium pyroarsenate or as the pentasulphide.

Hehner (*Analyst*, 1902, 27, 268) has shown that boiling hydrochloric acid does not bring about any considerable reduction and consequent volatilisation of arsenic acid, the effect observed by earlier investigators being due to the reducing action of organic matter introduced inadvertently through the use of cork or india-rubber stoppers. His results indicate that when the materials are kept as far as possible out of contact with organic matter the action of hydrochloric acid on arsenic acid is so much diminished that the distillates do not yield any arsenious sulphide on treatment with hydrogen sulphide, although giving plain indications of traces of arsenic when treated by the Marsh-Berzelius method.

A similar result was obtained with the apparatus now described, and as the amount of quinquevalent arsenic reduced and volatilised by hydrogen chloride is inconsiderable, the process affords a method for separating, at least approximately, the arsenic present in the two states of combination.

Mixtures of pure arsenious oxide and crystallised magnesium ammonium arsenate in known proportions were distilled first in hydrogen chloride alone and then in this gas mixed with hydrogen sulphide, the gaseous mixture being introduced at this stage by means of a glass T-piece fitted on to the inlet tube *a*.

The first precipitate of arsenious sulphide represented the tervalent arsenic and the second the quinquevalent condition. The sulphide derived from the former was formed quite as readily and quantitatively as when the pure arsenious oxide alone was employed; that obtained by reducing the arsenate contained more uncombined sulphur and was accordingly dissolved and oxidised by alkaline hypobromite, the arsenic being finally estimated as magnesium pyroarsenate.

Ferrous ammonium sulphate, zinc, and iron were also tried as reducing agents in the second stage of the distillation, but were found to be less satisfactory than hydrogen sulphide, as they sometimes caused a deposition of elemental arsenic which remained undissolved in the distilling flask, even when the operation was greatly prolonged.

In the presence of an antimonious salt, a certain quantity of the arsenate undergoes reduction on distillation in hydrogen chloride, the amount volatilised increasing as the proportion of antimony is augmented.

## II. *The Estimation of Carbon by Oxidation with Chromic Acid.*

It has been found that phosphoric acid may be substituted for hydrochloric acid with advantage in the indirect estimation of carbon dioxide in native carbonates by loss of weight (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 76). It is now shown that, in the direct method, the use of the non-volatile acid effects a simplification, since it renders unnecessary the employment of the safety tube containing pumice impregnated with anhydrous copper sulphate. Moreover, when the carbonate contains organic matter, the carbon in this material may be estimated by adding chromic acid to the residue and repeating the distillation, when the second increase in weight of the tared absorption tube indicates the organic carbon.

The efficacy of this process was tested in the following manner; the apparatus employed being of the ordinary form (Thorpe, *ibid.*, p. 84; Clowes and Coleman, *Quantitative Chemical Analysis*, ed. 1903, p. 122), excepting that an empty U-tube was interposed between the distillation flask and the sulphuric acid tube in order to condense some of the water driven off towards the close of the operation.

Mixtures of pure calcite and definite organic substances in known proportions were heated first with 25–35 c.c. of phosphoric acid (sp. gr. 1.75), and the carbon dioxide from the carbonate thus estimated. Chromic acid in moderate excess (3–4 grams) was now added and the flask containing the mixture heated on a fusible metal-bath, the temperature of which was gradually raised to 230–260°. About 30 minutes were required for the first distillation and 45 for the second.

0.6960 calcite + 0.1142 sucrose gave  $\text{CO}_2 = 51.57$  (from calcite) and  $\text{C} = 5.72$  (from sucrose), the calculated amounts being  $\text{CO}_2 = 51.54$  and  $\text{C} = 5.93$  respectively.

0.7120 calcite + 0.1440 phthalic acid gave  $\text{CO}_2 = 49.85$  and  $\text{C} = 9.68$ , the calculated amounts being  $\text{CO}_2 = 49.90$  and  $\text{C} = 9.67$  per cent.

0.7800 calcite + 0.1431 phthalic acid gave  $\text{CO}_2 = 50.59$  and  $\text{C} = 8.94$ , the calculated amounts being  $\text{CO}_2 = 50.66$  and  $\text{C} = 8.96$  per cent.

The last two results were obtained by different experimenters.

In view of the foregoing data, it seemed quite practicable to replace sulphuric by phosphoric acid in Ullgren's method of estimating the total carbon in cast iron, thus obviating the risk of absorbing in the

weighed tube any acid fumes resulting from the volatilisation or reduction of a portion of the sulphuric acid.

Wiborg (*Stahl und Eisen*, 1887, 465) and Blair (*J. Amer. Chem. Soc.*, 1896, 18, 223) have employed mixtures of chromic, sulphuric, and phosphoric acids, but in the latter case the amount of carbon dioxide evolved was determined volumetrically.

Two estimations of carbon in a sample of ferromanganese by this process gave the carbon as 7.26 and 7.17 per cent., whilst the combustion method gave 7.08. The carbon may be precipitated either in copper sulphate or copper ammonium chloride solution, and in order to oxidise the amount obtained from about a gram of ferromanganese, 25 c.c. of phosphoric acid (sp. gr. 1.75) and 4 grams of chromic acid are employed, the distillations are continued for an hour, the temperature of the metal-bath being gradually raised during the operation until it finally reaches 260°.

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### CIII.—*The Constitution of Hydrastinine.*

By JAMES JOHNSTON DOBBIE, D.Sc., F.R.S., and CHARLES KENNETH TINKLER, Research Student of the University of Edinburgh.

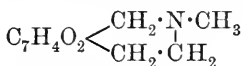
HYDRASTININE,  $C_{11}H_{13}O_3N$ , a derivative of the alkaloid hydrastine, is closely related to cotarnine, from which it differs only in being without the methoxyl group which is present in the benzene nucleus of the latter substance.

The main points in the constitution of these two substances have been satisfactorily determined by the study of their chemical reactions, but the data thus obtained are insufficient to allow of a decision being arrived at as to which of the formulæ proposed by different chemists should be assigned to the alkaloids in the solid state or in solution in any particular solvent.

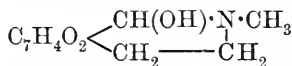
In a former paper (*Trans.*, 1903, 83, 598), evidence, drawn from an examination of the absorption spectra of cotarnine and its derivatives, was adduced in favour of the adoption of Decker's carbinol formula for this substance in the solid state and in solution in ether or chloroform. If this evidence is accepted as satisfactory in the case of cotarnine, it follows from the known relations of the two compounds that hydrastinine must be represented by a similar formula, but in view of the remarkable character of some of the results obtained

with cotarnine, it seemed to us desirable to make an entirely independent examination of hydrastinine.

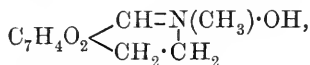
Hydrastinine is a colourless, crystalline substance which is soluble in anhydrous, alcohol-free ether or chloroform to a colourless solution,\* but with water or alcohol it yields a yellow, fluorescent solution. The absorption spectra of the colourless and coloured solutions are entirely different, the former being practically identical with those of hydrohydrastinine, a compound which is generally considered to have the constitution represented by formula (I), the latter with those of the hydrastinine salts. It may, therefore, be assumed that hydrastinine and hydrohydrastinine are constituted alike, and that the carbinol formula (II), which represents the former as being derived from the latter substance (I) by the replacement of an atom of hydrogen by hydroxyl, is to be preferred to Roser's open chain or aldehydic formula, which leaves the agreement between the spectra of the two substances unexplained. On the other hand, the identity of the absorption spectra of the aqueous or alcoholic solutions of hydrastinine with those of the hydrastinine salts shows that in these solvents hydrastinine possesses the quaternary ammonium form (III).



(I) Hydrohydrastinine.



(II) Hydrastinine (carbinol form).



(III) Hydrastinine (ammonium form).

The spectra exhibited by solutions of hydrastinine and hydrastinine derivatives agree closely with those of the corresponding solutions of cotarnine and its derivatives.

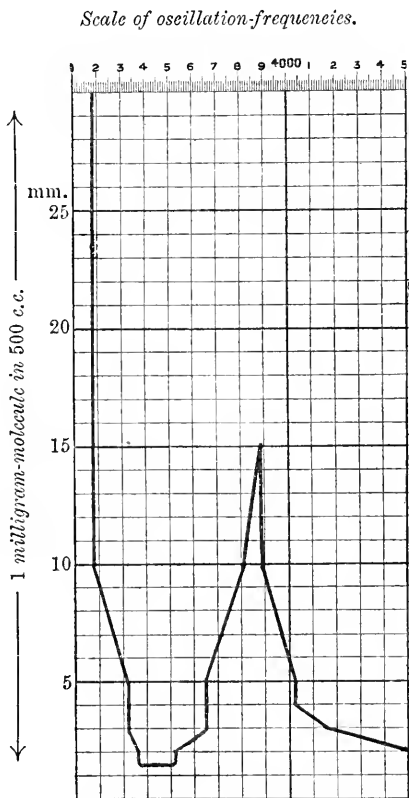
1. The spectra of the colourless solutions have one band in the same position as the band of colourless solutions of cotarnine. The general absorption exhibited by these spectra is, however, slightly greater than that of the corresponding cotarnine spectra, the difference being nearly the same as between the spectra of the parent alkaloids, hydrastine and narcotine (Trans., 1903, 83, 605). Solutions of hydrastinine in ether or chloroform, hydrohydrastinine and its salts, cyanohydrohydrastinine in solution in ether or chloroform, cyanohydrohydrastinine methiodide, and methoxyhydrohydrastinine methiodide possess spectra of this type.

All these substances are colourless, and can be represented, con-

\* There is no reason to suppose that either ether or chloroform exercises any chemical action on hydrastinine, which can be recovered from these solvents without alteration. The absorption spectra of these solutions are therefore regarded as the absorption spectra of the solid substance.

sistently with their known reactions, by means of the carbinol formula.

2. The spectra of dilute aqueous or alcoholic solutions of hydrastinine\* show, on the other hand, a large amount of general absorption, and possess three absorption bands. One of these corresponds in position with the band of cotarnine at the extreme ultra-violet end of the spectrum, whilst the other two together occupy the position of the cotarnine band which is nearest to the visible end of the spectrum. In other words, one of the cotarnine bands is represented in the hydrastinine spectra by two narrower bands. Apart from this difference, the agreement between the spectra of aqueous solutions of cotarnine and hydrastinine is very close. All the true salts of hydrastinine possess the same spectra as the aqueous or alcoholic solutions of hydrastinine. The solutions which give these spectra are all yellow and fluorescent, and the substances may be represented by the quaternary ammonium formula, in which the nitrogen atom is linked to an adjacent carbon atom by a double bond. It should be added that the spectra of a solution obtained by removing the chlorine from an aqueous solution of hydrastinine hydrochloride by means of silver oxide are identical with those of the chloride, whereas the spectra of a solution obtained by the addition of an excess of caustic soda to hydrastinine hydrochloride are identical with those of hydrastinine in ether.

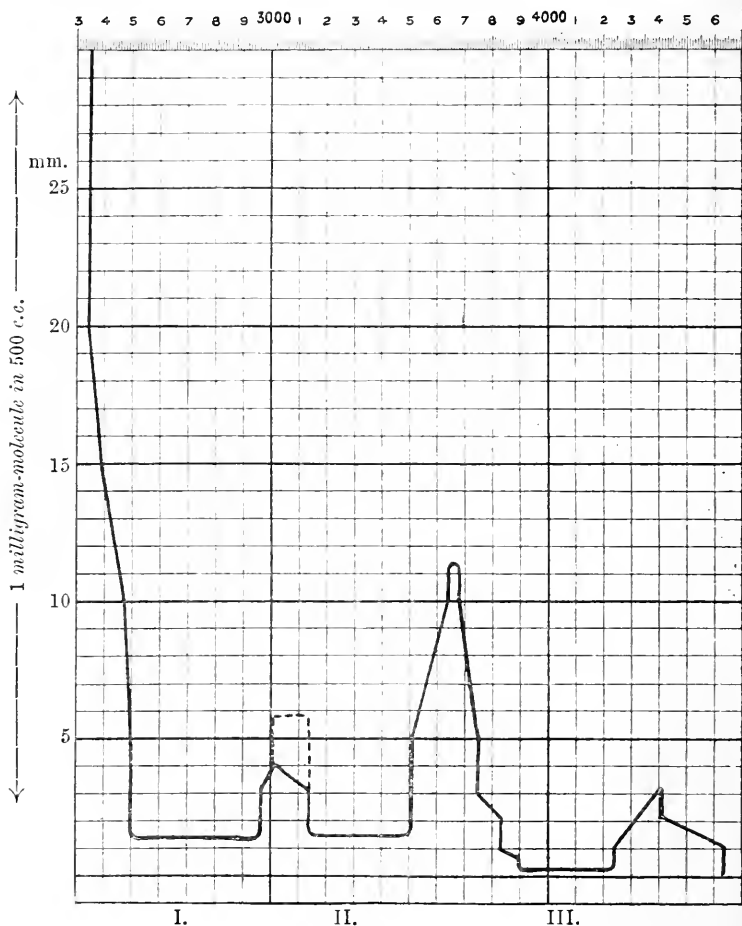


CURVE I.

\* The absorption curve of hydrastinine in alcohol, given in a former paper (Trans., 1903, 83, 605), was drawn before it was known that the constitution of this substance is altered by solution in alcohol. The curve really represents the absorption caused by a mixture of the carbinol and quaternary ammonium forms.

As in the case of cotarnine, the argument in favour of assigning the carbinol formula to solid hydrastinine and its colourless solutions derives

*Scale of oscillation-frequencies.*



*Hydrastinine hydrochloride.*

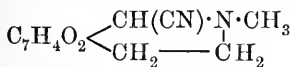
The curve of hydrastinine in water is coincident with the curve of hydrastinine hydrochloride except where indicated by the dotted line.

The numbers I, II, and III denote the positions of the absorption bands referred to in the text.

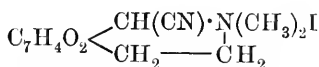
CURVE II.

confirmation from the study of the cyanide. By the interaction of hydrastinine hydrochloride and potassium cyanide in aqueous solution,

a colourless compound (m. p. 80—81°) is obtained, which differs in its slight solubility and other properties from the true salts of hydrastinine, and cannot, therefore, be represented by a similar formula. This substance, moreover, like cyanohydrocotarnine, forms a methiodide, the constitution of which can only be satisfactorily explained by regarding the cyanide as a derivative of hydrohydrastinine or of the carbinol form of hydrastinine (IV and V).

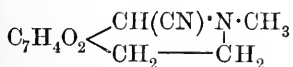


(IV) Cyanohydrohydrastinine.

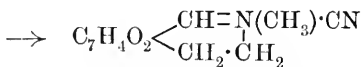


(V) Cyanohydrohydrastinine methiodide.

As has already been pointed out, the spectra of both these substances are identical with those of the other colourless derivatives of hydrastinine. Cyanohydrohydrastinine, it should be mentioned, is less stable than cyanohydrocotarnine, for whilst the latter substance dissolves in alcohol as well as in ether or chloroform to a colourless solution, alcohol colours the former yellow, changing it partly into true hydrastinine cyanide.



Cyanohydrohydrastinine.



Hydrastinine cyanide.

The proportion of hydrastinine cyanide to cyanohydrohydrastinine is increased by the addition of more alcohol and diminished by the presence of an excess of potassium cyanide.

Alcohols act on solid hydrastinine or on an ethereal solution of hydrastinine in the same way as on cotarnine.

When hydrastinine is dissolved in a small quantity of alcohol, the solution, on being examined with the spectroscope, is seen to consist of a mixture of the carbinol and quaternary ammonium forms of the substance. By adding more alcohol or by raising the temperature, the proportion of the quaternary ammonium form is increased. The proportions of the two forms present under any given conditions can be ascertained with considerable accuracy by comparing the photographs of their spectra with a series of photographs of the spectra of solutions containing the two forms mixed in known proportions (Trans., 1903, 83, 598, Plate III). The action of methyl alcohol is similar to that of ethyl alcohol, but under the same conditions a given quantity of the former transforms a larger amount of the carbinol form into the ammonium base than an equivalent quantity of the latter. Under the influence of alkalis, the quaternary ammonium form of hydrastinine is changed into the carbinol modification. The amount of change depends principally on the amount of alkali, and is practically the same for molecular quantities of the fixed bases. The action of

bases on molecular quantities of hydrastinine and cotarnine effects a greater change in the former than in the latter case.

Thus a solution of cotarnine in  $N/10$  caustic soda contains 90 per cent. of the carbinol form and 10 per cent. of the quaternary ammonium form, whilst an equivalent amount of hydrastinine dissolved in caustic soda of the same strength contains 95 per cent. of the carbinol form and 5 per cent. of the quaternary ammonium form. On the other hand, under the influence of alcohols, cotarnine changes more readily than hydrastinine from the carbinol to the quaternary ammonium form.

For example, a solution of cotarnine in methyl alcohol containing 1 mg. mol. in 500 c.c. contains 70 per cent. of the carbinol and 30 per cent. of the quaternary ammonium form, whilst a similar solution of hydrastinine contains 80 per cent. of the carbinol and 20 per cent. of the quaternary ammonium form.

Solutions of the ammonium form of hydrastinine are, as has been already stated, yellow, but the colour is less intense than that of the corresponding cotarnine solutions. They are, unlike the cotarnine solutions, strongly fluorescent. The fluorescence affords an excellent means of ascertaining whether or not a hydrastinine solution is free from the quaternary ammonium form, since it disappears at once when the conversion into the carbinol form is complete.

We have to express our thanks to Professor Crum Brown for kindly affording us facilities for carrying on this work in the University laboratory.

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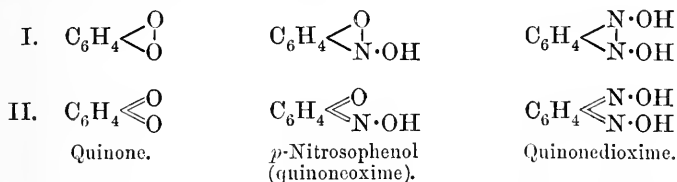
#### CIV.—*The Absorption Spectrum of p-Nitrosodimethylaniline.*

By WALTER NOEL HARTLEY, D.Sc., F.R.S.

IN the course of an investigation on the structure of compounds, such as quinone, *p*-nitrosophenol (quinoneoxime), and quinonedioxime, which are closely connected with the organic dyes, it was remarked that there are some features which the three absorption curves of the foregoing substances show in common, namely, an intense and widely extended absorption band, and that *p*-nitrosophenol (quinoneoxime) appeared to stand in an intermediate position between the other two. This may be seen on referring to the curves of the molecular absorption of the

three substances in the original paper (*British Association Report*, Belfast, 1902, Hartley, Dobbie, and Lauder, p. 107).

The constitutional formulæ for these quinone derivatives were written both with the peroxide structure (I) and also with the alternative so-called "quinonoid" formula (II):



For *p*-nitrosophenol we have also the formula  $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{OH} \\ \diagdown \text{NO} \end{smallmatrix}$ , usually employed for para-substituted phenols.

Evidence of the structure of such substances which is based exclusively on chemical reactions is inadequate for the purpose of establishing such formulæ, more particularly when the chemical properties of some of the substances are accounted far more satisfactorily when expressed by formulæ of another type. So powerful an oxidising substance is quinone, that the formula of a peroxide is more consistent with this property than that which is usually employed (Ciamician and Silber, *Ber.*, 1901, 34, 1350). The examination of its spectrum and those of its derivatives also affords evidence in favour of the peroxide constitution, for it must be under-

stood that the "quinonoid" formula  $\text{:C} \begin{smallmatrix} \diagup \text{C} \cdot \text{C} \\ \diagdown \text{C} \cdot \text{C} \end{smallmatrix} \text{C:}$  does not contain the benzene ring, but such a modification of it as is found in hydro-aromatic substances. This modification does not show selective absorption or even a very powerful absorption of any description, whereas quinone and quinonedichloroimide show powerful absorption bands such as one would expect to find in substances in which the linking of the carbon atoms is not less than that indicated by the formula

$\cdot \text{C} \begin{smallmatrix} \diagup \text{C} \cdot \text{C} \\ \diagdown \text{C} \cdot \text{C} \end{smallmatrix} \text{C} \cdot$ . Whether a ring of the form  $\text{O} \cdot \text{C} \begin{smallmatrix} \diagup \text{C} \cdot \text{C} \\ \diagdown \text{C} \cdot \text{C} \end{smallmatrix} \text{C} \cdot \text{O}$  or  $\cdot \text{N} \cdot \text{C} \begin{smallmatrix} \diagup \text{C} \cdot \text{C} \\ \diagdown \text{C} \cdot \text{C} \end{smallmatrix} \text{C} \cdot \text{N}$  is, by reason of the double linking of O: and ·N: atoms to the carbon ring, endowed with properties similar to those of aromatic derivatives, we have at present no means of determining.

All that can be accepted is, that the substances which we know as quinone and quinonedichloroimide do show such absorption, and this powerful absorption in the ultra-violet is closely associated with the production of colour. The *p*-nitrosophenol (quinoneoxime) appeared to exhibit peculiar properties, which were judged to be probably characteristic of the presence of the nitrosyl group attached to the

benzene ring. To ascertain whether this was actually the case, the following work was commenced. It had already been shown that the absorption bands in the spectrum of quinone, of which there are two, appear in solutions of two different dilutions; that is to say, the first band in the less refrangible part of the ultra-violet disappears on dilution before the second band makes its appearance. These bands in the ultra-violet are exclusive of any absorption in the visible spectrum, which, it may be remarked, is not very definite or characteristic.

It will suffice to quote the following figures, which refer to the ultra-violet:

*Quinone*, 1 milligram-molecule in 100 c.c. of water.

Thickness of liquid layer = 5 mm.; 1st band from  $1/\lambda$  3148 to 3568 ( $\lambda$  3176 to 2802).

1 milligram-molecule in 500 c.c. of water.

Thickness 2 mm.; 2nd band from  $1/\lambda$  3824 to 4411 ( $\lambda$  2615 to 2267).

It will be seen that these bands are not very broad, but the second one is very intense. Thus with the original solution diluted twenty-five times and contained in a cell 2 mm. thick, the second band is seen between  $1/\lambda$  3886 and 4240 ( $\lambda$  2573 and 2358); and there is still a strong absorption down to a dilution of 1 milligram-molecule in 12,500 c.c. of water.

*p-Nitrosophenol* (quinoneoxime) shows two broad absorption bands in the same dilution, over and above any absorption of the visible spectrum, which is not very definite or important:

Thickness, 1 milligram-molecule in 500 c.c.

4 mm. 1st band from  $1/\lambda$  2714 to 3886 ( $\lambda$  3684 to 2573).

3 mm. 1st band „ 2768 to 3824 ( $\lambda$  3612 to 2615).

2nd band „ 3886 to 4321 ( $\lambda$  2573 to 2314).

The 1st band is the most persistent, for with 3 mm. of a solution containing 1 in 2,500 c.c. it is seen extending from  $1/\lambda$  3148 to 3491 ( $\lambda$  3176 to 2864).

*Quinonedioxime*.—This has only one band, but it is very broad, rather like a fusion of the two bands in the *p*-nitrosophenol spectrum, and it is more persistent.

Thickness, 1 milligram-molecule in 100 c.c.

2 mm. Band from  $1/\lambda$  2744 to 4321 ( $\lambda$  3644 to 2314).

1 milligram-molecule in 2,500 c.c.

1 mm. Band from  $1/\lambda$  3148 to 3295 ( $\lambda$  3176 to 3034).

It has already been shown that open chain oximes, for instance,

aldoxime and acetoxime, have no exceptional absorption intensity (Hartley and Dobbie, *Trans.*, 1900, 77, 318—327); it seemed, therefore, desirable to ascertain whether nitroso-compounds of benzene derivatives exhibited a characteristically powerful absorption and whether they differed in any particulars from the oximes.

Eduard Kock has examined the visible spectra of eleven closely related nitrosoanilines, which are all coloured substances (*Ann. Phys. Chem.*, 1887, 32, 167—171). These compounds belong to a class which, the author justly remarks, has but few members, but their optical properties are peculiar in this respect, that they show absorption extending through the red at one end and through the blue at the other, so that only the borders of darkness on each side of the transmitted rays are available for measurement. His measurements were made through three different thicknesses of solutions containing gram-molecular proportions in 100 grams of alcohol, and measuring 4·3 mm., 8·6 mm., and 12·9 mm. The substituted nitrosoanilines follow the rule that where substitution is effected by alkyl radicles, the general form of the absorption curve will be the same for all, although differing in small details, in individual substances, as we know is the case in numerous other instances.\* Where the substitution takes place in the amino-group the result will be less appreciable than where the hydrogen atoms of the benzene ring are replaced, but in this substance also we can calculate what the effect on the curve will be. Hence, by examining one such compound thoroughly, we obtain information as to the nature of the absorption in the others. By selecting a compound in which two alkyl radicles replace the hydrogens in the  $\text{NH}_2$  group of the aniline, the possibility of substitution occurring elsewhere than in the benzene ring is precluded. By this means, the maximum absorption due to the position of the  $-\text{NO}$  group is placed under observation; for, in every instance hitherto recorded, the area enclosed by the curve where it marks the position of the absorption is greater in the case of the para- than in that of either the ortho- or meta-derivatives, although the position of the band may not extend so far down into the less refrangible part of the spectrum; an instance of this is afforded by *p*-hydroxybenzoic acid. This is shown in the diagrams of the *o*- and *p*-toluidines, the three xylenes, the isomeric cresols, dihydroxybenzenes, and hydroxybenzoic acids (*Trans.*, 1885, 47, 685; 1888, 53, 641).

In view of these facts, *p*-nitrosodimethylaniline was selected for examination. The action of boiling caustic alkali resolves it into

\* Hartley, "A Study of Coloured Substances and Dyes," *Trans.*, 1887, 51, 153; Hartley, Dobbie, and Lauder, *Brit. Assoc. Report*, Belfast, 1902, *ibid.*; J. Formánek, *Spektralanalytischer Nachweis künstlicher organischer Farbstoffe*, 1900, p. 5.

dimethylaniline and quinoneoxime (*p*-nitrosophenol) (Baeyer and Caro, *Ber.*, 1874, 7, 809); and therefore the relationship of these compounds appeared to afford a possible means of ascertaining whether there was a decided difference between the absorption curves of the *p*-nitroso-compounds and those of the very closely connected oximes. Quinonedioxime seems to absorb the visible and ultra-violet in a manner very similar to the quinoneoxime, but with greater intensity. The two curves resemble each other more closely than those of the quinone-chloroimides, and at the same time bear a strong similarity, although between corresponding oximes and chloroimides there is only the difference of the *o*-hydroxyl and chlorine radicles. Kock's measurements indicated the existence of a similar curve for all the nitroso-anilines, although his readings, made by the eye and not by photography, do not represent so intense an absorption on either side of the visible rays. It is best to photograph with isochromatic plates sensitive to the rays in the green and yellow. His measurements ( $\lambda$  604—511) of *p*-nitrosodimethylaniline agree with those recorded by me ( $\lambda$  6006—5111). But in both the quinoneoximes the widely extended and intense absorption observed to prevail, chiefly in the ultra-violet region, is shifted down towards the red in the case of the alkyl-substituted *p*-nitrosoanilines. When the substance had been prepared and its spectra photographed, a communication made by Professor W. R. Wood on the optical properties of this substance and the method of observing them was published (*Phil. Mag.*, 1903, [vi], 5, 257). This, however, had no reference to its chemical constitution, the results recorded having no obvious relation to the molecular weight of the substance.

#### EXPERIMENTAL.

The *p*-nitrosodimethylaniline employed in these measurements was specially prepared for the purpose by Mr. J. W. Wren, A.R.C.Sc.I., and one series of photographs was taken by him. The details of the spectra are recorded in oscillation-frequencies and wave-lengths, in addition to which a diagram of the curve is presented, which shows the relationship of the absorption in the visible region to that in the ultra-violet. To facilitate references and enhance the value of the scale, the solar lines from *A* to *T* have their positions indicated. The line *A* is as far in the red as can be well measured, whilst *H* and *K* lie in the extreme violet. The strength of solution and thicknesses of layer of liquid, which absorb and transmit various parts of the visible and ultra-violet spectrum, are clearly shown. The ordinates to the curve are drawn on a different scale to those of the British Association Report on the quinoneoximes, but there is no difficulty in comparing them.

*Description of the Spectrum of p-Nitrosodimethylaniline.*

0.150 gram in 100 c.c. of absolute alcohol, or 1 milligram-molecule.

Thickness of layer of liquid.

Rays transmitted

Scarcely visible.

mm.  
30, 25, 15, 10  
5
 $\frac{1}{\lambda}$ .  
1695—1922 |  
1665—1956 |  
 $\lambda$ .  
5899—5202 |  
6006—5112 |

0.150 gram in 500 c.c.

Absorption band.

 $\frac{1}{\lambda}$ .  
1956 to 2991 | 5112 to 3343 |  
1956 „ 2885 | 5112 „ 3466 |  
1956 „ 2839 | 5112 „ 3522 |

Rays transmitted

 $\frac{1}{\lambda}$ .  
2991—3079 | 3343—3247 |  
2885—3157 | 3468—3167 |  
2839—3376 | 3522—2962 |

0.150 gram in 2,500 c.c.

 $\frac{1}{\lambda}$ .  
2040 to 2735 | 4901 to 3656 |  
2040 „ 2710 | 4901 „ 3690 |  
2132 „ 2627 | 4690 „ 3806 |

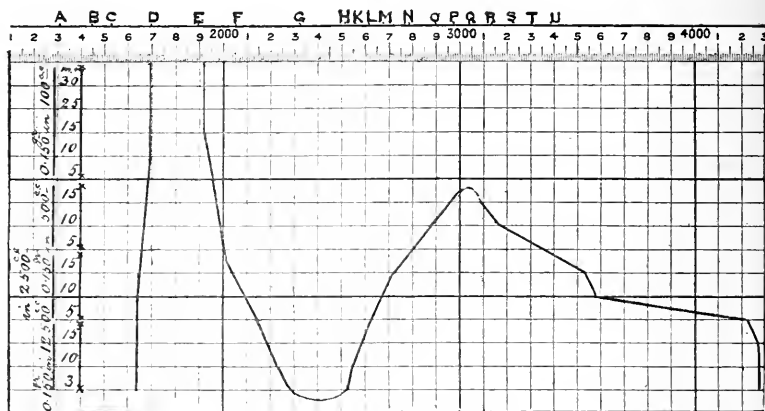
 $\frac{1}{\lambda}$ .  
2735—3537 | 4901—2827 |  
2710—3550 | 4901—2816 |  
2627—4235 | 4690—2361 |  
Feeble | Feeble |

0.150 gram in 12,500 c.c.

 $\frac{1}{\lambda}$ .  
2142 to 2600 | 4668 to 3846 |  
2172 „ 2551 | 4604 „ 3920 |

 $\frac{1}{\lambda}$ .  
2600—3668 | 4668—2726 |  
2551—3668 | 4604—2726 |  
Extension feeble from | Extension feeble from |  
3668 to 4266 | 2726 to 2344 |

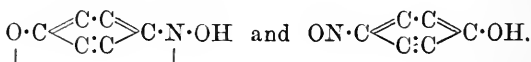
 $\lambda$ .  
1665—2142 | 6006—4668 |  
1665—2172 | 6006—4604 |  
1665—1753 very feeble to 1923 and from 1923 to 4266 (5200 to 2344) strong

*Scale of oscillation-frequencies.**p*-Nitrosodimethylaniline.*Conclusions.*

(1) The absorption caused by *p*-nitrosodimethylaniline at the less refrangible end of the spectrum extends into the infra-red, and at the more refrangible end it goes far into the ultra-violet. This restricts the transmitted rays to a continuous spectrum composed only of yellow and green light, which is bordered on either side by a band of intense darkness. This is characteristic of *p*-nitroso-compounds, the edge of the band in the blue shifting according to the number of hydrogens replaced and the nature of the radicles engaged in the substitution.

(2) There appears to be a decided difference in constitution between the quinoneoxime (*p*-nitrosophenol) and *p*-nitrosodimethylaniline, which cannot be accounted for by a substitution of OH for N(CH<sub>3</sub>)<sub>2</sub>, because the widely extended and intense absorption band which belongs to quinoneoxime (*p*-nitrosophenol) is, in the case of the *p*-nitrosodimethylaniline and its congeners, shifted along from the ultra-violet far down into the visible region.

(3) The alkyl-substituted phenols and anilines absorb varying quantities of the ultra-violet, the absorption not extending into the visible spectrum, but the introduction of the NO as distinguished from the N·OH group extends the absorption far into the coloured rays. This is a characteristic effect of the nitrosyl group, which, when it replaces hydrogen in the benzene ring, constitutes a chromogen. From this it appears to be not improbable that a solution of *p*-nitrosophenol is a mixture of the two tautomeric forms:



(4) Although the absorption of rays in the blue and violet by *p*-nitrosodimethylaniline is strong, there is at a certain dilution a transmission of the greater part of the ultra-violet. This fully explains the results obtained by Wood, which are somewhat difficult to understand from the description of his experiments, since he leaves out of consideration both the strength of solution and thickness of layer of liquid which will absorb and transmit various parts of the visible and ultra-violet rays respectively. He describes the preparation of a screen made from a mixture of *p*-nitrosodimethylaniline and magenta, which is found to transmit the ultra-violet rays, whilst it absorbs all that are visible. In a paper published some years ago ("Researches on the Relation between the Molecular Structure of Carbon Compounds and their Absorption Spectra. Part VIII," Trans., 1887, 51, 153—202), which dealt chiefly with triphenylmethane and azobenzene and also their respective derivatives, a number of curves derived from these substances is given. With respect to their properties, it was stated that when a strong absorption occurs in the visible spectrum, the ultra-violet is also absorbed, and that there appeared to be but little hope of obtaining a strongly coloured substance which would transmit the ultra-violet. When any single compound is examined, this still appears to be the case. From the curve given, it will be seen that the green and yellow rays are the only parts of the spectrum not absorbed, and, although an absorption of other rays is intense, yet the amount of green and yellow transmitted has great luminosity; in other words, the compound is not darkly coloured. Kock's experiments were made with solutions ten times as strong as mine, and they could not, therefore, through any thickness examined by him, transmit the ultra-violet.\* On examining the measurements which I have already given, it is shown that with a solution 5 mm. thick containing 0.150 gram in 2,500 c.c. of alcohol, practically all the ultra-violet is transmitted from wave-length 3818 to 2372. There is an absorption between wave-lengths 4690 and 3818, with transmission of the rays between 6006 and 4690; it is necessary, therefore, if it is desired to make an effective screen transmitting only the ultra-violet, to find some absorbent medium for this part of the spectrum which will at the same dilution transmit the ultra-violet. These being chiefly yellow and green rays, a red solution suitably diluted, so as not to absorb beyond wave-length 3818, should be employed. A milligram-molecule or 0.3375 gram of rosaniline hydrochloride dissolved in 2500 c.c. of alcohol and 1 mm. thick absorbs from  $\lambda$  5740 to 4870, whilst transmitting all the more refrangible rays, as may be seen from the diagram for this substance (*loc. cit.*) and the tabulated state-

\* It should be noted that, apparently, Kock took 115 to be the molecular weight of *p*-nitrosodimethylaniline instead of 150.

ment of measurements. When these solutions placed in two different cells were tested by an arc light, it was found that some red rays were transmitted, but it is possible to adjust the thicknesses of the solutions so that what appears to be darkness causes the fluorescence of uranium nitrate and barium platinocyanide to be brilliantly exhibited when a quartz lens is used. The appearance was brightest when some feeble blue rays were transmitted. The difference between what was observed by the eye in the one case, and by photography in the other, is due to the feeble photographic power of the red transmitted rays.

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### CV.—*The Electrolytic Estimation of Minute Quantities of Arsenic.*

By HENRY JULIUS SALOMON SAND, Ph.D., M.Sc., and JOHN EDWARD HACKFORD.

THE estimation of minute quantities of arsenic has been improved in rapidity and reliability during the last few years by the practical application of electrolysis to the liberation of hydrogen and arsenic trihydride in place of the chemical method adopted in the Marsh-Berzelius test.

Already in 1861 an electrolytic method was described by Bloxam (Quart. Jour. Chem. Soc., 1861, 13, 12, and 338), but owing, largely no doubt, to the inconvenience of obtaining electrical energy from galvanic batteries—the only source practically available in those days—the method does not seem to have been generally adopted.

Since the epidemic of poisoning in Lancashire in 1900 due to accidental contamination of beer with arsenic, the testing of brewing materials for this poison has become a matter of considerable practical importance, and several chemists have carried out experiments with the electrolytic method.

Details of the application of this method in his laboratory were published by Trotman in July, 1902, in the *Brewers' Journal*, 1902, 445.

In consequence of the appointment of the Royal Commission on Arsenical Poisoning, the electrolytic process was carefully investigated in the Government Laboratory, and a method for the electrolytic estimation of minute quantities of arsenic, more especially in brewing materials, was described by Thorpe in August, 1903 (*Trans.*, 1903, 83, 974).

These investigators employed platinum cathodes, with this difference,

however, that Trotman recommends the addition of zinc sulphate to the electrolyte under examination.

In Thorpe's communication, special attention is drawn to the fact that arsenates are not reduced in his apparatus. He therefore recommends that the substance under examination should be treated with nascent sulphurous acid before introduction into the electrolytic vessel. The same preliminary treatment was recommended by Bloxam, who also clearly recognised the difficulty of reducing arsenates electrolytically. Even the effect of mercury in hindering the detection of arsenic, which has been fully examined in the present investigation, was already pointed out by Bloxam, and a method for dealing with solutions containing arsenates in presence of antimony and mercury was elaborated by him.

In Trotman's communication no preliminary treatment of the material examined is recommended, and no mention is made of the difficulties due to the presence of arsenates. As will be seen from the present paper, however, a platinum electrode in the presence of zinc sulphate as recommended by Trotman behaves as a zinc electrode and is capable of reducing arsenates. In fact, the authors are in a position to state that both platinum and zinc electrodes were experimented on by Trotman, the former being unsatisfactory whilst the latter gave satisfactory results. Owing to the obvious inconvenience of employing a soluble electrode composed of a material not easily obtained free from arsenic, the zinc electrode was, on the recommendation of one of the authors of the present paper, replaced by one of platinum electrolytically coated with zinc by the addition of zinc sulphate to the electrolyte under examination.

Since the completion of the following investigation the use of zinc electrodes for arsenic testing has been recommended by Mr. W. Thomson, who also finds that arsenates are reduced by them (*Mem. Manchester Phil. Soc.*, May, 1904, 17, 48.)

In the present investigation, the manner in which the nature of the electrode and other conditions affect the production of hydrogen arsenide by electrolysis of arsenates and arsenites has been fully examined, and as a result suggestions have been made for the further simplification of the electrolytic estimation of minute quantities of arsenic, and certain possible sources of error in the method are indicated.

The influence of the material of the cathode may be classified under the two headings of "supertension" and catalysis. The supertension ("Ueberspannung." Caspari, *Zeit. physikal. Chem.*, 1899, 30, 89) of an electrode is the excess of electromotive force necessary for the liberation of hydrogen at that electrode over the electromotive force required for the reversible production of hydrogen on a cathode of

platinised platinum. As is well known, this excess is due to the resistance offered to the production of gas bubbles in the liquid, and varies with the nature of the electrode in contact with it. Hydrogen evolved with a high supertension, possessing a large amount of free energy, has the thermodynamic properties of enormously compressed gas, and before its liberation in bubbles the layer of liquid immediately adjoining the electrode as well as the metal of the electrode itself no doubt becomes enormously supersaturated with the gas. As a result, such hydrogen is capable of effecting reductions requiring a large amount of free energy, and it has, for example, been shown by Tafel (*Zeit. physikal. Chem.*, 1900, 34, 227) that the reduction of caffeine depends to a very large extent on the supertension of the electrode employed. The supertension (in volts) of the most important metals having been determined by Caspari (*loc. cit.*) in Nernst's laboratory in the following order: platinised platinum, 0.005; smooth platinum, 0.09; nickel, 0.21; copper, 0.23; tin, 0.53; lead, 0.64; zinc, 0.70; mercury, 0.78, it is possible to predict, with a fair amount of certainty, the behaviour of an electrode during reduction with regard to this effect.

The thermodynamic efficiency of electrolytic hydrogen, which is limited by the magnitude of the supertension of the electrode, is, however, not the only influence determining electrolytic reduction. Catalytic effects due to the metal of the electrode, and often also to substances in solution, play an important part as well, and these catalytic effects may vary in different cases, and can, therefore, not be predicted like those due to supertension.

In the present case, we have been able to show that the reduction of very small quantities of arsenate to arsenite probably requires a large supertension, for this was only accomplished by the metals having a large supertension, such as lead, zinc, and also by iron in the form of wire.\* Platinum, on the other hand, which has a low supertension, proved inefficient even for very considerable concentrations of arsenates. The production of hydrogen arsenide from arsenites, however, depends on other influences besides supertension, for this could be accomplished with smaller concentrations of arsenious acid when platinum electrodes were employed than when those of copper with a much larger supertension were used. Moreover, mercury electrodes, having the highest supertension of all the metals, proved to be utterly inefficient. As will be seen in the sequel, it was possible to reduce arsenates or arsenites by their means to metallic arsenic, but impossible to convert the latter into arsenic trihydride. Even the production of arsenic trihydride from arsenites, however, seems

\* The supertension of iron in acid solution has not been recorded by Caspari, but its efficiency as an electrode agrees with Tafel's observation.

to require a certain amount of supertension, for when electrodes of platinum coated with platinum black were employed, none of the trihydride was produced. This circumstance corresponds with Thorpe's observation that platinum electrodes become inefficient when they are roughened by prolonged use.

The apparatus employed for the experiments was, with the exception of the electrodes, identical with the form recommended originally by Trotman. A diagram illustrating the modification recommended by us with lead electrodes is given at the end of the present paper. The cathode chamber consisted of a glass cylinder, 3 to 4 cm. in diameter and 16 cm. in height, closed at one end by a porous partition of parchment paper,\* at the other by an india-rubber bung, through which passed the electric connection to the electrode, a tap funnel for the introduction of the liquid to be examined, and a thermometer. The evolved gases passed through a side-tube into a drying tube containing a cotton wool plug, calcium chloride, and lead acetate paper, and then through the Marsh-tube.

Where not specially stated to the contrary, the anode consisted of a platinum band; the cathode of the metal examined had as nearly as possible the same effective surface in all experiments, being either a rod, hollow cylinder, or spiral of about 2 cm. in diameter and 3 cm. in height. The strength of the current which was taken from the lighting mains through a lamp resistance was 5—6 amperes. The electrolyte in all the experiments on acid solutions was a 10 per cent. solution of sulphuric acid. A blank experiment lasting twenty to thirty minutes was always performed before the standard solution containing the arsenic was introduced. The latter was made up in various strengths with sodium hydrogen arsenate for the experiments on arsenates and with arsenious oxide for those on arsenites. Experiments were at first carried out under the ordinary working conditions with the apparatus surrounded by ordinary cold water. In this case, the temperature in the cathode compartment varied from 15—50°. Experiments were then made at 0—5°, pieces of ice being placed in the anode and cathode compartments; and, lastly, the temperature of the cathode compartment was raised to about 97°, the liquid in the anode compartment being heated to boiling. All the recorded determinations were repeated at least once. Preliminary experiments showed that with a non-sensitive electrode, the whole of the arsenic is not removed from the solution as arsenic trihydride, the mirror obtained corresponding in intensity with only a part of the arsenic. Thus, when a spiral of copper wire was employed as a cathode and 0.00001 gram of arsenious oxide was added, a mirror corresponding with only half that

\* For the advantages of a parchment-paper partition, see Trotman, *J. Soc. Chem. Ind.*, 1904, 23, 178.

quantity was obtained. On changing the Marsh-tube after this and continuing the passage of the current, no more arsenic was deposited; when, however, small quantities of the oxide were added, these additions were detected in full. It may therefore be concluded that each electrode will only detect quantities of arsenic above a certain lower limit peculiar to itself, and that it is possible to compare the efficiency of electrodes by comparing the sizes of mirrors obtained after the introduction of the same initial amount of arsenic. The standard mirrors for these experiments were prepared in an electro-

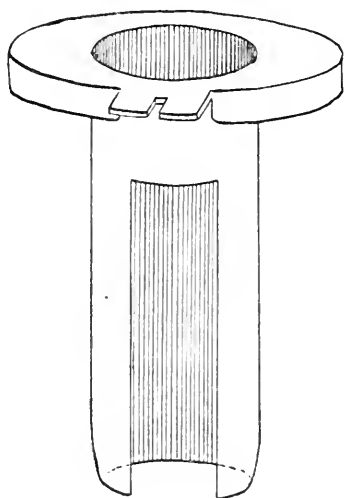


FIG. 1.



FIG. 2.



FIG. 3.

lytic apparatus with platinum electrodes, the arsenic being added in the arsenious state.

The Tables I, II, and III show the results obtained, quantities being stated in terms of 0.000001 gram of arsenious oxide. The details regarding the electrodes are as follows:

Tables I and III, electrodes of single metal.

Platinum: hollow cylinder, height 4 cm., diameter 2 cm.

Platinised platinum: same electrode coated with platinum black, according to Lummer and Kurlbaum (Kohlrausch und Holborn, *Leitvermögender Elektrolyte*, p. 9).

Copper: spiral of  $1\frac{1}{2}$  mm. wire, height and diameter the same as the platinum cylinder.

Iron: spiral of pure thin wire wound round glass rods, height and diameter approximately the same as above.

Zinc: solid cylinder of the shape illustrated in Fig. 2, diameter and height as above.

Lead: same shape as zinc. (1) With ordinary smooth surface, (2) roughened by alternate electrolytic oxidation and reduction.

Mercury: contained in small flat crystallising dish of about 3 cm. diameter, the current being introduced by means of platinum wire fused into a glass tube.

Table III. Platinum electrode as above, 10 c.c. of 10 per cent. solutions, or, where this was not possible, of saturated solutions of the salts stated in the table, having been added to the electrolyte.

The main features of the results revealed by the tables have already been summarised, but certain points called for further investigation. The most important of these was the lack of efficiency of the mercury electrode in spite of its high supertension. A quantity of 0.0001 gram of arsenic was therefore introduced into the apparatus in the state of arsenate, the cathode being mercury. After the current

TABLE I.

Experiments with minute quantities of arsenic. Solid cathodes. Quantities stated in terms of 0.000001 gram of  $As_2O_3$ .

Electrode.	Arsenite added.	Arsenite detected.	Temperature.	Duration of experiment in minutes.	Arsenate added.	Arsenate detected.	Temperature.	Duration of experiment in minutes.
Platinum (smooth) .....	5	5	0—5°	35	5	0	0—5°	30
	5	2	97	30	5	0	97	30
Copper .....	6	1	0—5	30	6	1	0—5	30
	6	1	97	30	6	1	97	30
Iron .....	5	5	0—5	30	5	5	0—5	30
	5	5	97	30	5	5	97	30
Lead (smooth) .....	5	5	0—5	30	5	5	0—5	30
	5	5	97	45	5	5	97	45
Lead (roughened).....	5	5	0—5	30	5	5	0—5	30
Zinc.....	5	5	0—5	30	5	5	0—5	20
	5	5	97	30	5	5	97	20
Mercury .....	5	0	0—5	30	5	0	0—5	30
	5	0	97	30	5	0	97	30

TABLE II.

Experiments with platinum cathode coated electrolytically with other metal by the addition of a salt solution. Quantities of arsenic in terms of 0.000001 gram of  $\text{As}_2\text{O}_3$ .

Salt added.	Arsenite		Temperature.	Arsenate		Temperature.
	Added.	Detected.		Added.	Detected.	
$\text{CuSO}_4$ .....	6	1	0—5°	5	0	15—50°
$\text{FeSO}_4$ .....	5	5	„	1	0	„
$\text{PbAc}_2$ .....	5	5	„	1	1	„
$\text{ZnSO}_4$ .....	5	5	„	1	1	„
$\text{HgCl}_2$ .....	5	0	„	1	0	„
$\text{NiSO}_4$ .....	—	—	—	1	0	„

TABLE III.

Experiments with inefficient electrodes and larger quantities of arsenic, approximate limits below which arsenic was not detected. Quantities stated in terms of 0.000001 gram of  $\text{As}_2\text{O}_3$ .

Electrode.	Arsenite, limit.	Arsenate, limit.	Temperature.
Platinum (smooth)	— —	200 200	0—5° 97
Platinum (platinised)	above 500 „ „	above 500 „ „	0—5° 97
Mercury	3000—5000 „ „	3000—5000 „ „	0—5° 97

had passed for five minutes the mercury was removed, carefully washed with water, and then shaken thoroughly with some bleaching powder solution, one-third of the latter being then tested for arsenic in the usual manner, when the mirror obtained was too intense for accurate estimation. Careful blank experiments had been made with the mercury and other chemicals to prove their original freedom from arsenic. This experiment proves that the difficulty in the use of a mercury electrode is not to be found in its incapacity to reduce arsen-

ates to metallic arsenic, but in the difficulty of converting the latter into arsenic trihydride. No doubt this is largely due to the fact that the arsenic dissolves in the mercury, and thus to a great extent escapes the action of the nascent hydrogen.

The conclusion drawn was further confirmed by an experiment in which 0.00004 gram of arsenic was added, and the current passed for 1 hour. No mirror was obtained, but nevertheless all the arsenic must have been reduced to the metallic state, and thus removed from the liquid, for when the latter was tested it was found to be quite free from arsenic.

The cause of the inefficiency of copper as an electrode for quantities of arsenate and arsenite below about 0.000005 gram of arsenious oxide was also investigated more closely. For this purpose a quantity of 0.00001 gram of the oxide was introduced into the apparatus and electrolysed for two hours with a copper cathode. A mirror corresponding in intensity with only about half the substance added was obtained. All the arsenic had nevertheless been removed from the liquid, for when the latter was examined by means of the lead apparatus recommended at the end of the paper it was found to contain no arsenic. The same experiment was then carried out with the single difference that sodium arsenate was substituted for the arsenious oxide. In this case, however, all the arsenic was not removed from the solution, for when the latter was tested in the lead apparatus it gave a mirror corresponding with about 0.000002 gram of arsenic. It may, therefore, be concluded that a copper cathode will completely reduce arsenious acid, but that part of the arsenic reduced remains as metallic arsenic, and is not converted into arsenic trihydride. On the other hand, probably owing to lack of sufficient supertension, arsenates are not completely reduced by means of a copper electrode.

The experiments recorded in Table I show that the electrodes most sensitive for very minute quantities of arsenic in the state of arsenate are those of lead, zinc, and iron (as wire). The last two being soluble in the electrolyte are manifestly inconvenient for practical use. Lead, on the other hand, being insoluble both as an anode and as a cathode is an exceedingly suitable metal. Its cheapness is an additional advantage, and when carefully selected it is possible to obtain commercial samples absolutely free from arsenic and antimony. The experiments of Table II demonstrate the correctness of the principle underlying Trotman's method that platinum electrodes may be employed for the detection of minute quantities of arsenic in the state of arsenate when zinc salts are added. Lead salts may also be employed but are less convenient, owing to the precipitate of lead sulphate which is formed when they are introduced into the electrolyte. Iron salts do not affect the platinum electrodes either for the detection of

arsenates or arsenites. This may perhaps be due to the difficulty of obtaining a deposit of iron on the platinum.

In order further to test the suitability of lead as an electrode for the detection of arsenic, various substances, such as mineral and vegetable oils and metallic salts were added to the electrolyte. The

TABLE IV.

Experiments with a lead cathode and anode with various added substances. Ordinary working temperature 15—50°. Quantities in terms of 0.000001 gram of  $As_2O_3$ .

Substance added.	Arsenite		Arsenate	
	Added.	Detected.	Added.	Detected.
Vaseline in ether .....	1	1	1	1
Olive oil .....	1	1	1	1
Olive oil in ether .....	1	1	1	1
$ZnSO_4$ .....	1	1	1	1
$CuSO_4$ .....	5	0	1	0
$HgCl_2$ .....	1	0	5	0
$FeSO_4$ .....	1	0	5	0
$Sn(NH_4)_2Cl_6$ .....	1	0	10	0
$NiSO_4$ .....	1	0	—	—
$CuSO_4$ + $PbAc_2$ .....	5	5	1	1
$FeSO_4$ + $PbAc_2$ .....	5	5	1	1
$NiSO_4$ + $PbAc_2$ .....	—	—	1	1
$HgCl_2$ + $PbAc_2$ .....	1	0	5	0

oils were without effect, but as was to be foreseen the metallic salts, excepting those of lead and zinc, render the electrode inefficient. Their influence can, however, be neutralised by the simultaneous addition of a solution of lead acetate (or zinc sulphate) in all cases except where mercury salts were present. Extreme caution is therefore necessary if mercury is employed for making electric connections, for special experiments showed that so small a quantity as one centigram of mercuric chloride is sufficient to destroy utterly the sensitiveness of an electrode. Table IV. shows the results of experiments.

A final series of experiments was carried out with electrodes of lead, zinc, and platinum in alkaline solutions (25 per cent. solutions of caustic soda). The lead and zinc cathodes were not sensitive under these conditions, and those of platinum were utterly useless. The lower limit, which could be detected at 0° and 100° with solutions of

arsenites and arsenates was about 0.000015 gram for lead and zinc, and about 0.002 for platinum.

As a result of the foregoing investigation, we are able to recommend the use of lead electrodes for the detection of minute quantities of arsenic by electrolysis. The appended figures will explain the apparatus in the form in which it is in use in Mr. Trotman's laboratory in Nottingham at the present time. With slight modifications it has been employed for about four months with unvarying success; about 1800 determinations having been made. During a fortnight all results were checked, firstly, by electrolysis in an apparatus with platinum electrodes, the substance examined having been previously reduced with potassium metabisulphite and sulphuric acid according to Thorpe's process, and, secondly, they were checked according to Trotman's method in an apparatus with a platinum cathode, zinc sulphate (in some cases also lead acetate) being added. Upwards of 140 determinations were checked in this manner, the results obtained by the three methods being in every case identical. The apparatus is extremely sensitive, it being possible to detect with certainty 0.0000005 gram of arsenic in 50 c.c. of liquid. As examples of the use of the apparatus we give the methods employed for the estimation of arsenic in malt and beer.

**Malt:** forty grams are thoroughly shaken in a beaker with 100 c.c. of a 10 per cent. solution of sulphuric acid and heated on the water-bath for 20 minutes with occasional shaking, the beaker being covered, and the temperature not being allowed to rise above 50—60° in order to minimise evaporation. Fifty c.c. of the solution are then introduced into the apparatus, a few drops of amyl alcohol being added to prevent frothing. Half an hour is allowed for the total deposition of the arsenic.

**Beer:** ten c.c. of strong  $\text{H}_2\text{SO}_4$  are added to 50 c.c. of the beer, and introduced into the apparatus, together with a few drops of amyl alcohol, half an hour being allowed for the deposition of the arsenic.

#### *Details of Apparatus.*

FIG. 4. *A.* Cooling vessel for water, conveniently replaced by an insulated lead trough, when several sets of this apparatus are being used simultaneously.

*B.* Anode compartment.

*C.* Anode of lead (view in Fig. 1), lid-shaped, to minimise spraying of acid, with a slot to allow cathode to be observed, height 5", inner diameter 2", bent inwards at the bottom to support the cathode compartment, the latter being conveniently placed on a glass-rod triangle (not shown in figure) to allow bubbles of oxygen to escape more readily.

*D.* Cathode compartment, glass cylinder, width 1½", height 7", closed at one end by an india-rubber stopper, at the other end by arsenic-free parchment paper, tied

while wet by means of string and kept in its place by the flange on the end of the cylinder.

*E.* Cathode of pure lead, solid. Height 1", thickness  $\frac{3}{4}$ ". Length of stem 7". View in Fig. 2.\*

*F.* Funnel, with wide stem, having graduations of 10 c.c., 25 c.c., 50 c.c., closed by a ground-glass rod.

*G.* Drying tube charged with (*a*) lead acetate paper, (*b*) calcium chloride, and (*c*) plug of cotton wool.

*H.* Shield to protect bunsen burner from draughts. View in Fig. 3.

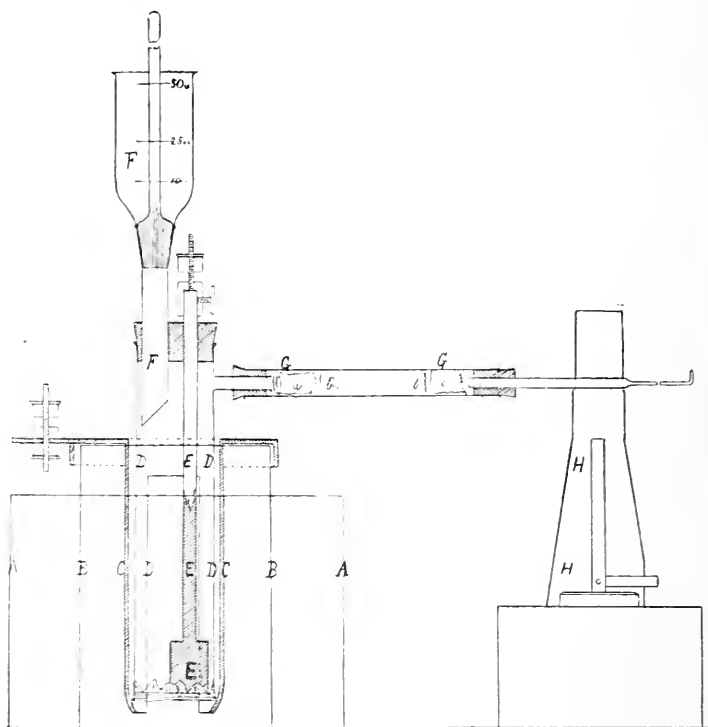


FIG. 4.

Current : about 5—6 amps., that is, for single apparatus 9—10, thirty-two candle-power lamps on a 260 volt circuit.

Electrolyte : anode solution : 10 per cent. sulphuric acid. Cathode solution : liquid under examination. Temperature, 15—50°.

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NOTTINGHAM.

\* As new cathodes often contain arsenic on the surface ; they should be thoroughly scraped and cleaned by immersion in boiling strong nitric acid for three or four minutes and subsequent washing with water. They should be perfectly bright, and give a negative result after a blank experiment lasting one hour.

CVI.—*The Ultraviolet Absorption Spectra of Certain Enol-keto-tautomerides. Part I. Acetylacetone and Ethyl Acetoacetate.*

By EDWARD CHARLES CYRIL BALY and CECIL HENRY DESCH, D.Sc.

IN consequence of the acid character of the methylene group in compounds of the type of acetylacetone or ethyl acetoacetate, such compounds give rise to a series of metallic derivatives in which one hydrogen atom is replaced by a metal. At least two structural formulæ are possible for each metallic derivative, according as the latter is regarded as being derived from either the ketonic or aldehydic, or from the enolic modification of the parent compound. In the earlier researches on the metallic derivatives of ethyl acetoacetate (Conrad, *Annalen*, 1877, 188, 269), the ketonic structure is adopted, the metal being represented as attached to carbon, thus,  $\text{CH}_3 \cdot \text{CO} \cdot \text{CHNa} \cdot \text{CO}_2\text{Et}$ . The chemical evidence derived from the action of reagents is inconclusive, but at the present time the enolic structure is generally adopted, the metal being attached to oxygen, as in the case of the metallic salts of acids and phenols. The evidence for this view has been summarised by W. Wislicenus ("Ueber Tautomerie," Stuttgart, 1897).

The sodium and potassium derivatives of  $\beta$ -diketones,  $\beta$ -ketonic esters, &c., are crystalline salts, dissolving readily in water, and dissociating in solution, at the same time undergoing extensive hydrolysis. Acids decompose them completely and instantaneously, setting free the undissociated parent compound.

In striking contrast with these unstable, readily dissociated alkali derivatives are the compounds containing weakly positive metals, such as aluminium and ferric iron. A number of such derivatives have been prepared by Claisen (*Annalen*, 1894, 281, 314), Combes (*Compt. rend.*, 1887, 105, 868; 1894, 119, 1221), Conrad (*Annalen*, 1877, 188, 269), and others, and show remarkable stability, being in many cases volatile without decomposition, so that their vapour densities have been determined (Kohler, *Amer. Chem. J.*, 1900, 24, 385). They also crystallise well from indifferent organic solvents. Their properties have been further investigated, and additional examples of the class prepared and described, in a paper by Hantzsch and Desch (*Annalen*, 1902, 323, 1). In this communication it is shown that solutions of the ferric and aluminium derivatives of acetylacetone, &c., are practically non-electrolytes and do not show the reactions of the metal, and that decomposition by acids only takes

place slowly, and does not proceed completely in the sense of the upper arrow, even in presence of a large excess of acid :



Conversely, when acetylacetone is added to a solution of ferric or aluminium chloride in water or alcohol, the conductivity rises considerably, owing to the formation of an undissociated metallic derivative and the setting free of hydrochloric acid. It is in consequence of this property that the intense colorations with ferric chloride which characterise many feebly acid organic compounds are produced, these colorations being stable even in presence of a large excess of mineral acid.

This marked difference in the properties of the alkali compounds and the aluminium and ferric derivatives suggested the possibility of a corresponding difference of constitution. The former class might be regarded as derived from the enolic form, and therefore as containing the metal attached to oxygen, and the latter from the ketonic form, and containing the metal attached to carbon. A similar explanation has been generally adopted in the case of certain mercury derivatives investigated by Ley and Hofmann, which show a similarly abnormal behaviour. Thus nitroform,  $\text{CH}(\text{NO}_2)_3$ , forms coloured alkali compounds with an oxygen linking, derived from the hypothetical  $\psi$ -nitroform, as  $\text{C}(\text{NO}_2)_2:\text{NO}_2\text{Na}$  (Hantzsch and Rinckenberger, *Ber.*, 1899, 32, 628), whereas the mercuric compound, which is white, does not give the reactions of mercury, and is therefore considered to contain a mercury-carbon linking,  $\text{CHg}_2(\text{NO}_2)_3$  (Ley and Kissel, *Ber.*, 1899, 32, 1357).

No definite conclusions can be drawn from the chemical reactions of the metallic derivatives with acetyl chloride, alkyl iodides, &c. The products obtained are in some cases *O*-derivatives, in others *C*-derivatives, frequently a mixture of the two, the actual conditions determining the nature of the substitution being probably very complex (Wislicenus, *loc. cit.*).

Determinations of the electrical conductivity of aqueous solutions of a number of metallic derivatives of acetylacetone and ethyl acetoacetate were made, and the extent of their decomposition by hydrochloric acid was ascertained. On comparing compounds of the same weak acid with a series of metals of decreasing positivity, if the same structure were common to all, there should be found a gradual transition from unstable, greatly dissociated and hydrolysed salts to inert, undissociated compounds. On the other hand, an actual difference in structure between the extreme terms of the series would be indicated by an abrupt break at some intermediate point, but no such discontinuity was found. The conductivities form a descending series, from

the sodium and potassium compounds, through magnesium and zinc, to aluminium and ferric iron at the other extremo. Thorium and beryllium group themselves with aluminium; lanthanum, a more strongly positive metal, forms a derivative of considerably higher conductivity than aluminium.

The present communication contains the results of the examination of the ultraviolet absorption spectra of acetylacetone and ethyl acetoacetate and of their metallic derivatives, an investigation undertaken with the view of determining the actual structure of these substances. This method, originally introduced by Hartley and Huntington (*Phil. Trans.*, 1879, 170, i, 257), has been largely applied by Hartley with Dobbie and others to the determination of the constitution of isomeric and tautomeric compounds.

We have adopted Hartley's method of work and have measured the amount of absorption occurring with different amounts of the various substances. Hartley has employed the electric spark between electrodes of alloys of tin, lead, cadmium, and bismuth as the source of illumination, and has photographed the spectrum of the light after it has passed through various thicknesses of solutions of the compounds. We have substituted the electric arc between iron poles for the electric spark, and have thereby gained some advantage both from its greater convenience and from the large increase in the number of lines in the spectrum, which conduces to more accurate reading of the limits of absorption.

An adjustable cell has also been used for containing the different solutions; this consists of two glass tubes, one of which slips easily into the other, as shown in Fig. 1. Both these tubes have

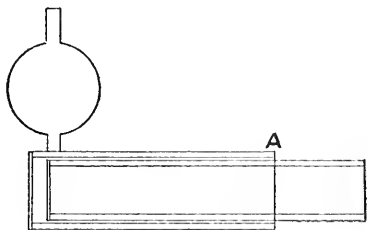


FIG. 1.

a flange at one end which is ground flat at right angles to the axis, and on this flange is cemented a quartz plate in each case. A broad india-rubber band is slipped over the junction at A, and serves to keep the vessel water-tight, whilst the inner tube can slide freely through this collar; in this way the thickness of solution dealt with can readily be altered. A millimetre scale is ruled on the outer tube so that the thickness of the solution can be read off directly. The great advantage of using such a cell, as against a number of cells of definite thicknesses, is obvious both from its greater convenience and also from the amount of time saved.

The actual thicknesses of solution used in the experiments were generally 30, 20, 15, 10, 5, and 4 mm., and if necessary these thick-

nesses were used again with the solution diluted to ten times its volume. It was found that with one exception the whole of the absorption band could be traced out by photographing the spectrum through the above thicknesses, first with  $N/500$ , and then with  $N/5000$  solution. In actual practice a tenth of a milligram-equivalent was dissolved in 50 c.c. of alcohol or distilled water, as the case might be; this was put in the absorption cell after carefully rinsing it with some of the solution, and the iron spectrum was photographed through the thicknesses quoted above, with an exposure in each case of fifteen seconds. If necessary, this solution was diluted to ten times its volume, and the spectrum again photographed. In this way a complete record of absorption was obtained for lengths, varying from 5 to 300 mm., with a  $N/5000$  solution.

The method of plotting the results requires some notice. In Hartley and Huntington's first paper on the ultraviolet absorption spectra of organic compounds the limits of absorption and transmission were read for every photograph, and the points so obtained, expressed in oscillation frequencies, were plotted against the equivalent volumes of solution, using a constant thickness of solution. In his more recent papers, Hartley, instead of volumes of solution, has used the equivalent thicknesses of a solution of constant concentration. In all the curves of absorption the oscillation frequencies are expressed on the abscissæ and the volumes or thicknesses on the ordinates. These two methods give very different results, for in the first case a definite change in the molecular concentration is represented by a larger change on the ordinates at lower concentrations than it is at higher concentrations; on the other hand, in the second method, a definite change in molecular concentration is represented by a smaller change on the ordinates at lower than it is at higher concentrations.

There seems therefore to be a certain disadvantage attaching to both these methods of representation. Judging from Hartley's and Hartley and Dobbie's numerous examples, it seems extremely probable that the persistence of an absorption band over a considerable range of concentration is one of its most important and characteristic functions. It is absolutely necessary to trace the absorption bands over the necessary range of dilution from their first appearance to their final disappearance. In comparing the absorption spectra of substances together, the change of concentration corresponding with the beginning and end of an absorption band is one of the most important factors. Using either of Hartley's methods a comparison of these concentration changes is not readily made from the curves; in one case the curves are too compressed at greater concentrations, and in the other they are too compressed at the lower concentrations. Some intermediate method seems desirable. It appears to us that a given relative

concentration change should be represented by the same change on the ordinates whatever may be the actual concentration. In these circumstances, a band which, for example, just persists while the concentration is halved should occupy the same space when plotted, whatever be the actual concentration. A better comparison between the various bands will then be possible. We have therefore expressed our results by plotting the logarithms of the concentrations or equivalent thicknesses; in this way passing from one ordinate to the next represents a definite relative change in the thickness; for example, in the curves shown this change amounts to 25 per cent. We venture to suggest that this method should be always adopted for the expression of spectroscopic results.\*

The first part of the work consisted in the determination of the absorption spectra of acetylacetone, and of its metallic derivatives. The beryllium, aluminium, and thorium compounds were used and the absorption in each case is shown by the curves in Fig. 2 (p. 1034). The figures on the left-hand side of the diagrams refer to the logarithms of the thicknesses, and those on the right to the thicknesses themselves, that is to say the equivalent thicknesses of a  $N/5000$  solution. It will be seen from Fig. 2 that all the curves have very much the same shape, and that there is a well marked absorption band in each case. Curve No. 1 is that of acetylacetone, whilst Nos. 2, 3, and 4 are those of the beryllium, aluminium, and thorium compounds respectively. These curves show distinctly that the constitution of the metallic derivatives is very closely allied to that of acetylacetone itself. Now Perkin (*Trans.*, 1892, 61, 800) has shown by means of his magnetic rotation experiments that acetylacetone probably consists of a mixture of 70 per cent. of the di-enolic modification with 30 per cent. of the mono-enolic form. It seemed at first as if we could only interpret the above results by considering the metallic derivatives to be enolic, that is to say, with the metal attached to the oxygen atom. This preliminary conclusion was also borne out by the results we obtained with ethyl acetoacetate and its aluminium derivative; the ester itself gave a small general absorption with no trace of a band, whilst the aluminium compound gave a strong banded absorption almost identical with the acetylacetone spectra. The curves are shown at Fig. 3, No. 2, and Fig. 4, No. 3. These results pointed to the fact that the ethyl acetoacetate was entirely of the ketonic form, whilst its aluminium derivative was entirely enolic. It may be pointed out that the specimen of ethyl acetoacetate gave a coloration with ferric chloride which developed extremely slowly, whilst the acetylacetone gave a strong coloration immediately.

\* Lord Rayleigh has suggested this method for expressing wave-lengths in spectroscopy (*Nature*, 1883, 27, 559).

Further consideration of these results with a view of explaining the meaning of the absorption bands in these compounds shows that there is absolutely no *a priori* reason why the enolic derivatives should have a band at all. From all Hartley's work there is indeed every reason to expect the contrary. It is well known that a double band exerts no banded absorption, neither does a hydroxyl group. Hence, neither

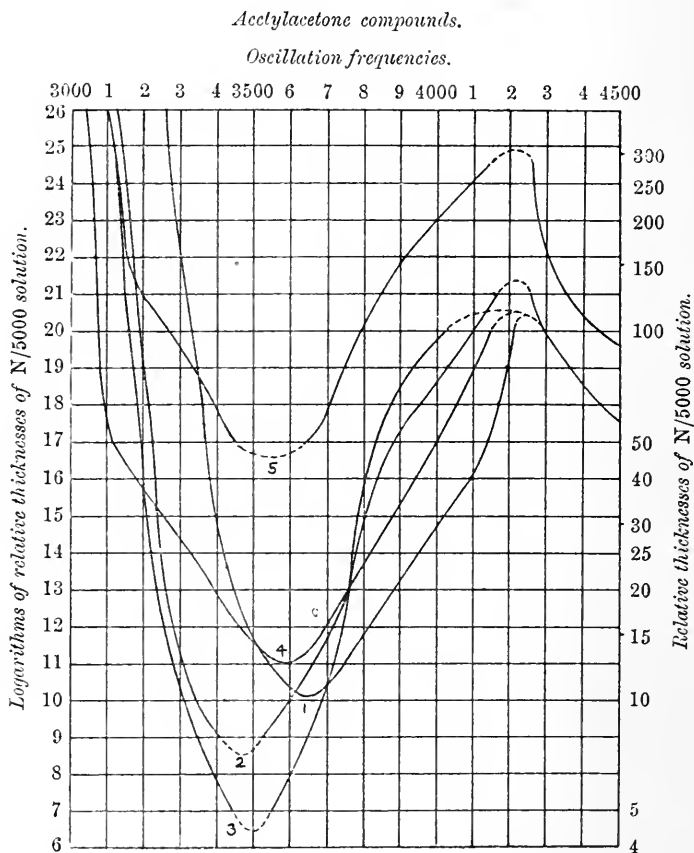


FIG. 2.

the enolic,  $-\text{C}(\text{OH})\text{:CH}-$ , nor the ketonic,  $-\text{CO}\text{:CH}_2-$ , group is likely to give rise to a band. The true explanation must be sought elsewhere. In order to decide this question, we observed the absorption spectra of the two ethyl derivatives of ethyl acetoacetate, namely, ethyl  $\beta$ -ethoxycrotonate,  $\text{CH}_3\text{:C}(\text{OEt})\text{:CH}\text{:CO}_2\text{Et}$ , and ethyl ethylacetoacetate,  $\text{CH}_3\text{:CO}\text{:CHEt}\text{:CO}_2\text{Et}$ . Solutions of these substances were made up of

the usual strength and their absorption spectra photographed.\* The absorption curve of the enolic form, ethyl ethoxycrotonate, is indicated

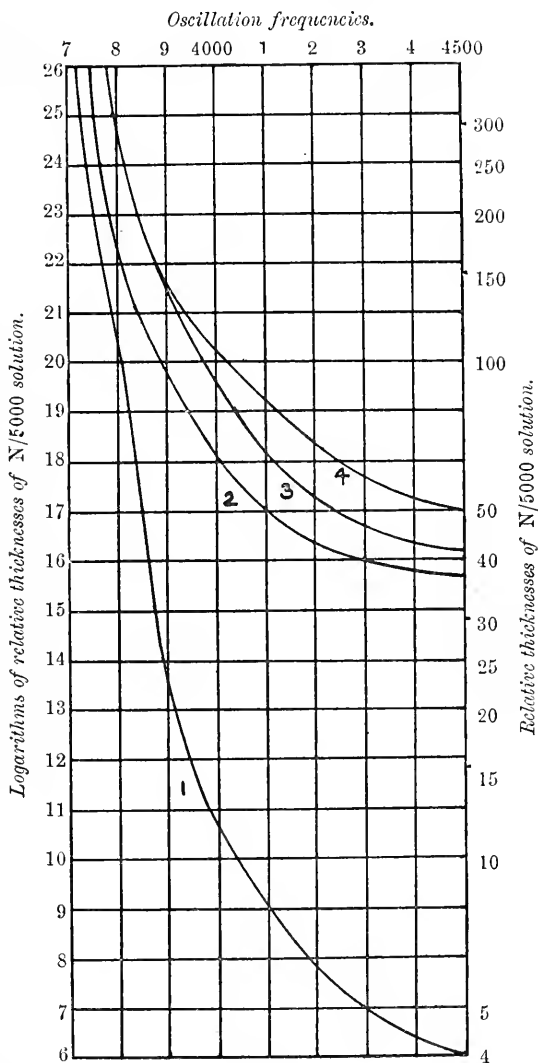


FIG. 3.

in Fig. 3, No. 1, and shows only general absorption with no trace of a band; the keto-substance, ethyl ethylacetoacetate, at the strength

\* We are indebted to Dr. Lapworth for the first of these compounds, and for the second to Professor Collie.

employed is practically quite diactinic. As Hartley alone, and also in conjunction with Dobbie, has frequently shown that the introduction of a light alkyl radicle does not modify the type of spectrum, these results leave no doubt that the spectra of the pure enolic and of the pure ketonic modifications show no band. Moreover, no band is produced by a mixture of the two ethyl derivatives, and it is, therefore, evident that the foregoing absorption bands are not due to any definite chemical structure.

An interesting confirmation of this lies in the fact that we obtained no absorption band in the spectrum of ethyl hydroxymethylene-succinate,\*  $\text{CO}_2\text{Et}\cdot\text{C}(\text{:CH}\cdot\text{OH})\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , in which a structure occurs almost identical with that of enolic compounds.

These results seem to justify the view that the absorption band is due to the vibration connected with the change from the one modification into the other. When the pure enolic and ketonic modifications are dealt with either alone or mixed together, there is no banded absorption; when, however, the molecules are oscillating from one condition to the other, then a band is produced. In these substances, we are dealing with some of the simplest possible forms of tautomerism, for they are purely fatty substances without the benzenoid structure which is always accompanied by absorption bands. It appears, therefore, that the simple dynamic isomerism occurring in these compounds gives rise to absorption bands, and it is not too much to expect that, generally speaking, absorption bands in all spectra of this type are due to some such isomerism.

To investigate this more fully we have studied the action of sodium hydroxide and of hydrochloric acid on ethyl acetoacetate. If the theory brought forward for the explanation of the absorption bands is correct, it is evident that sodium hydroxide should cause a band to appear in the spectrum of this substance, the length or persistence of which band should depend directly on the quantity of sodium hydroxide added. This follows from the fact that alkalis have been shown by Lapworth and others to increase the velocity of change between such isomerides, that is to say, they increase the number of molecules in the state of change. For exactly similar reasons, hydrochloric acid should have an opposite effect, owing to the restraining influence it is known to exert on certain of these changes.

In Fig. 4 (p. 1037) are shown the absorption curves obtained with solutions of ethyl acetoacetate in water containing sodium hydroxide; Curve 1 is the absorption curve of the ester with half an equivalent of sodium hydroxide, Curve 2 that of the ester with one equivalent of the alkali, and Curve 4 the same with an excess of alkali. Curve 3 shows the absorption of the aluminium compound. These curves indicate at

\* Our thanks are due to Miss Kahan, who kindly prepared this substance for us.

once the value of the new method of plotting, for the persistence of the bands is directly proportional to their height on the ordinates. Curve 1 shows that half an equivalent of sodium hydroxide produces an absorption band which persists when the relative thickness is halved; the addition of one equivalent of sodium hydroxide delays the appearance of the band, but the band now persists until the relative

*Oscillation frequencies.*

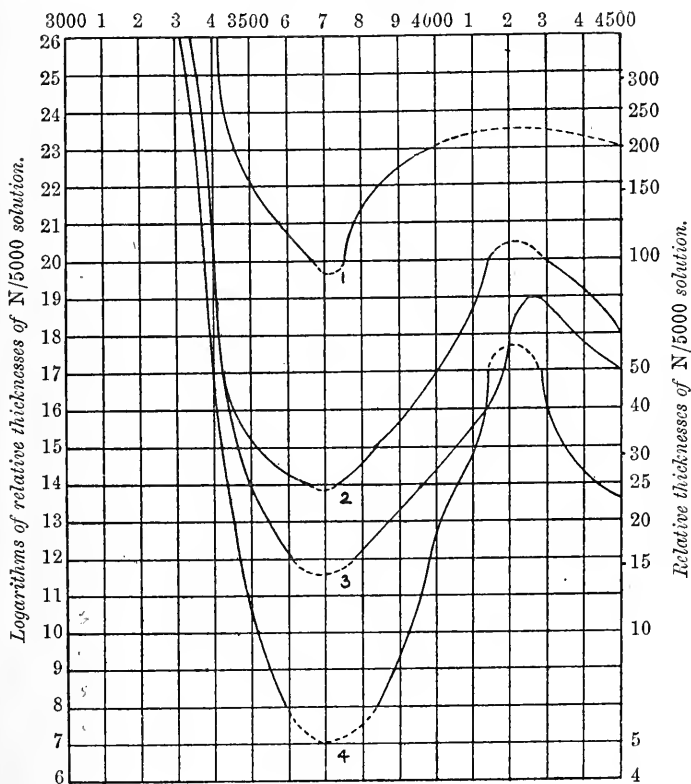


FIG. 4.

thickness is reduced to one-third. An excess of sodium hydroxide still further delays the band, but the band now persists until the relative concentration is reduced to one-tenth. It is interesting to note that an excess of sodium hydroxide develops a band which is considerably more persistent than that given by the pure aluminium salt in alcoholic solution. Perhaps this fact is the most striking evidence in favour of our views which can be brought forward.

As regards the action of hydrochloric acid, this is shown in Curves 2, 3, and 4, Fig. 3, in which No. 2 represents the ethyl acetoacetate alone, and Nos. 3 and 4 with a trace and excess of this acid respectively. It will be noticed at once how the addition of the acid decreases the absorption. These last results show that ethyl acetoacetate is not entirely ketonic, because there is some oscillation present which can be decreased by the addition of the hydrochloric acid. This is important, because the fact that the ester gives a coloration, although slowly, with ferric chloride points to the presence of some of the enolic modification.

The retarding action of hydrochloric acid is better shown in the case of ethyl  $\beta$ -aminocrotonate;\* the curves obtained with this substance being indicated in Fig. 5. Curve No. 3 is that of the pure substance in alcohol, No. 2 of the substance in alcohol with a trace of hydrochloric acid, whilst No. 1 is the same with excess of acid. The similarity between these curves and those showing the action of sodium hydroxide on ethyl acetoacetate is very striking. Hydrochloric acid has no action on acetylacetone.

These results leave little room for doubt that the absorption bands are due to the oscillation between the two isomerides, and we must therefore conclude that the metallic derivatives form equilibrium mixtures of the two possible forms, and that a constant rate of change is maintained from one to the other and back again. In the case of acetylacetone and its metallic derivatives, it will be seen from the curves that the positions of the absorption bands on the abscissæ are all very much the same; taking the two extreme cases of the beryllium compound and acetylacetone itself, the heads of the absorption bands lie at 3500 and 3650 respectively. It is perfectly evident that there is some vibration within the molecule of these substances which is in agreement with the frequency of the light rays absorbed. Therefore, in acetylacetone and in the beryllium, aluminium, and thorium derivatives, the vibration frequencies are the same within the limits 3500 and 3650; they may be considered as being practically of equal frequency, especially as they bear no relation to the molecular weights. It is difficult to conceive of a vibration common to all these compounds; it is impossible to consider the labile hydrogen and metal atoms as vibrating between the two carbon atoms, because their vibration frequencies could not be the same; for it must not be forgotten that the molecule of the thorium compound, for instance, must be regarded as being made up of a single thorium atom linked to four acetylacetone residues. The vibration may be connected in some way with the acetylacetone residue, but this again would be difficult

\* We are indebted to Professor Collie for this substance.

to understand, because, judging from other spectroscopic analogies, such vibrations would have a much lower frequency.

The absorption curves illustrating the action of sodium hydroxide on ethyl acetoacetate in Fig. 3, of hydrochloric acid on ethyl acetoacetate in Fig. 4, and on ethyl  $\beta$ -aminocrotonate in Fig. 5, show that the persistence of a band over the concentration changes may be

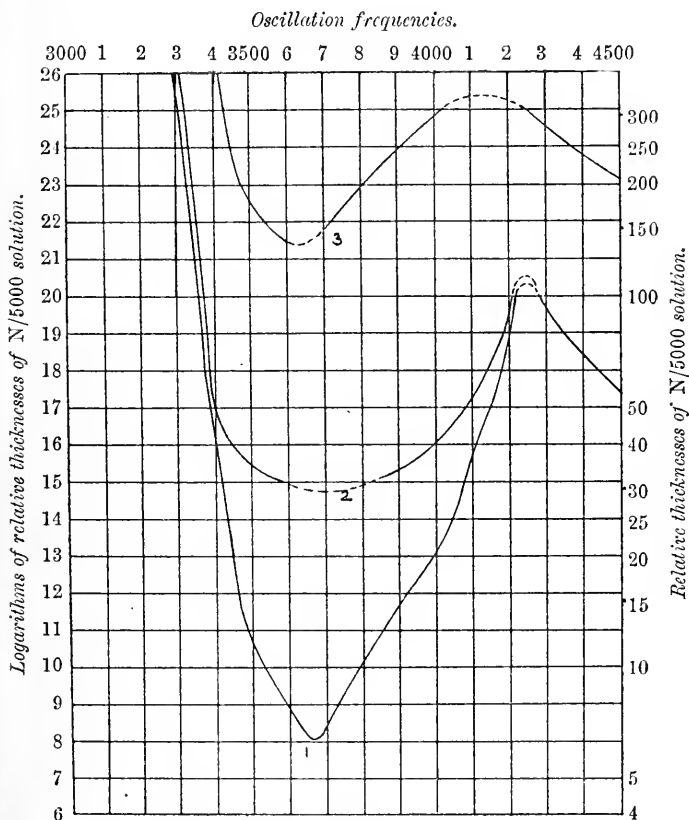


FIG. 5.

considered as a measure of the amount of chemical change occurring between the two tautomerides; in all probability it is a measure of the relative number of molecules in the transitory state. In these absorption bands it appears that we have a means at our disposal of determining the amount of reaction occurring between two substances which are in equilibrium with one another. Whatever is the view taken of the real origin of the bands, their relative persistence may

be looked on as a measure of the activity between the two isomerides; the velocity of change from one to the other must be constant and is not affected by sodium hydroxide or hydrochloric acid; no doubt it may be calculated from the frequencies of the heads of the absorption bands. These are 37,000 in the case of ethyl acetoacetate, 36,500 in the case of ethyl  $\beta$ -aminocrotonate, and in the case of the acetylacetone derivatives they lie between 35,000 and 36,500.

Now Perkin has found that acetylacetone probably exists to a great extent in the di-enolic condition; and in order to find out how far this double tautomerism is concerned in the absorption curves for this substance and its metallic derivatives, we measured the absorption spectrum of methylacetylacetone, in which there probably occurs only a single degree of freedom. The curve for this substance is shown in Fig. 2, and from its shape and persistence it seems that the acetylacetone curves are due to the double tautomerism, the effect of the second degree of freedom being to extend the persistence of the curves.

It is difficult to say how far the fact that the dynamic isomerism in acetylacetone and ethyl acetoacetate is the origin of the absorption band will influence the conclusions drawn by Hartley, and by this author and Dobbie, in regard to the constitution of the substances they have spectroscopically examined. The benzenoid structure has been frequently shown to give rise to absorption bands, and no doubt is the origin of the absorption bands in very many substances that have previously been investigated. There are two cases, however, in which possibly a slightly different interpretation may be put on the results from that which the authors have given. These are the ethyl dibenzoylsuccinates and the two isomerides of dibenzoylmethane. The former have been examined by Hartley and Dobbie (*Trans.*, 1900, 77, 498), and two types of spectra were found, one with general and continuous absorption, and the other with two absorption bands. These authors attributed the first type to the ketonic modification, and the second to the enolic form. The present results would, however, incline us to the view that the bands were due to the dynamic isomerism between the two forms, and not to the pure enolic modification. In the case of dibenzoylmethane and its enolic form,  $\alpha$ -hydroxybenzylideneacetophenone (*British Association Report*, 1901, p. 211), these two compounds gave spectra which appear somewhat similar, each having two absorption bands. The absorption bands of the one compound are sufficiently near in position to those of the other to justify the conclusion that the dibenzoylmethane was not entirely ketonic, and that  $\alpha$ -hydroxybenzylideneacetophenone was not solely enolic; it appears rather as if dynamic isomerism were present in both instances, but more pronounced in the case of  $\alpha$ -hydroxybenzylideneacetophenone.

These interpretations are not very different from those advanced by Hartley and Dobbie, but in the light of our results they are, we believe, more satisfactory.

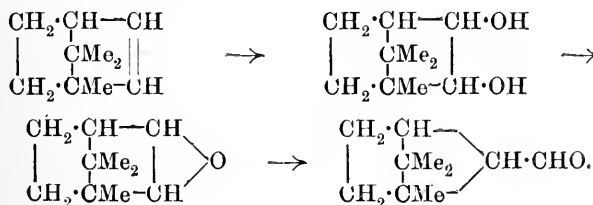
In conclusion, we wish to express our thanks to Professor Collie for the valuable help he has given us, and to Dr. Lapworth for the great interest he has taken in the experiments.

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## CVII.—*The Action of Chromyl Chloride on Stilbene, Styrene, and Phenanthrene.*

By GEORGE GERALD HENDERSON and THOMAS GRAY.

THE action of chromyl chloride on hydrocarbons has been the subject of much experimental work, but its behaviour towards unsaturated compounds has been comparatively little studied. Étard (*Compt. rend.*, 1893, 116, 434), Bredt and Jagelki (*Annalen*, 1899, 310, 112), and the authors (*Trans.*, 1903, 83, 1299) have examined the products of the oxidation of representatives of the terpenes by chromyl chloride, but the reactions in these cases are complicated by the presence of methyl groups in addition to the double linking, and difficulty is experienced in separating and identifying the resulting substances. In the case of camphene, Bredt and Jagelki (*loc. cit.*) conclude that the double linking is the point of attack and that the methyl groups remain unaffected. They suppose that the solid additive compound, which is formed by the action of chromyl chloride on the hydrocarbon, is converted by water into a dihydric alcohol which immediately loses the elements of water and undergoes a molecular rearrangement resulting in the formation of the aldehyde which they isolated :—

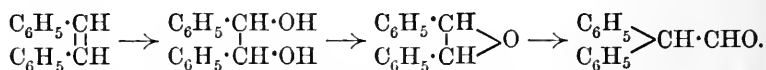


With the object of testing this hypothesis, and also of gaining an insight into the mechanism of the reaction which might throw some

light on the nature of the action of chromyl chloride on the terpenes which we are at present investigating, we have examined the behaviour of stilbene, styrene, and phenanthrene towards that reagent. Ten per cent. solutions of the hydrocarbons (1 mol.) in dry carbon disulphide were used, and a ten per cent. solution of pure chromyl chloride (2 mols.) in the same solvent was gradually added, the liquid being kept cool during the process. Reaction took place readily in each case, a brown solid additive product being precipitated at once. The precipitate was collected, washed with carbon disulphide, and then decomposed with water to which a little sulphurous acid had been added in order to reduce any chromic acid which might be formed.

*Action of Chromyl Chloride on Stilbene.*—The solid additive compound when decomposed with water yielded a brown oily liquid and some resinous matter. The liquid was extracted with carbon disulphide, and, after removal of the solvent, purified by distillation in a current of steam. The oil which passed over with the steam was then fractionally distilled.

Assuming the reaction to take the course suggested by Bredt and Jagelki in the case of camphene, we should expect hydrobenzoin and diphenylacetaldehyde to be produced from stilbene, according to the following scheme:—



Both the oily liquid which passed over with the steam and the residue from the steam distillation were carefully examined for these substances, but without success. On the other hand, the oily liquid was proved to be a mixture of benzaldehyde, benzil, and benzophenone. On fractionating this liquid, the first fraction was found to consist of benzaldehyde (with a little benzoic acid). From the fraction boiling at 300—310° a phenylhydrazone and an oxime were prepared, which proved to be benzophenonephenylhydrazone (m. p. 134—136°) and benzophenoneoxime (m. p. 139—140°). From the fraction boiling above 320°, prismatic yellow crystals separated on cooling. This substance after further purification melted at 95°, and gave the following results on analysis:—

0.1674 gave 0.4920 CO<sub>2</sub> and 0.0724 H<sub>2</sub>O; C = 80.15, H = 4.80.

C<sub>14</sub>H<sub>10</sub>O<sub>2</sub> requires C = 80.00; H = 4.76 per cent.

The identification of this substance with benzil was completed by converting it into the monoxime melting at 113—114°.

The yields of the various substances were approximately as follows: Benzaldehyde 7 per cent., benzoic acid 1.5 per cent., benzil 4 per cent., and benzophenone 1.5 per cent.

Hence, in addition to the oxidation to benzil, a partial decomposition of the stilbene molecule was effected by the action of chromyl chloride, with the resultant formation of benzaldehyde and benzophenone.

*Action of Chromyl Chloride on Styrene.*—As with stilbene, a viscid brown liquid was obtained on decomposing the solid additive product with water, which was freed from resinous matter and purified in the same way as the oxidation products of stilbene. The product in this case consisted almost entirely of benzaldehyde. The oil which came over towards the end of the steam-distillation was allowed to oxidise spontaneously, and from the oxidation product, after repeated crystallisations in order to remove benzoic acid, a very small quantity of an acid was obtained, which melted at  $76^{\circ}$ , and possessed the characteristic odour of phenylacetic acid; the quantity obtained was not sufficient for analysis. From this observation, we conclude that phenylacetaldehyde was formed in very small proportion. The oil which distilled in steam yielded, in addition to benzaldehyde, an acrid yellow oil, the vapour of which attacked the eyes. This substance, which was probably a chlorinated product, was not further examined.

*Action of Chromyl Chloride on Phenanthrene.*—The solid additive compound of phenanthrene and chromyl chloride yielded a solid product on treatment with water. This was found to consist of phenanthraquinone, mixed with some resinous matter. No trace of any compound of an aldehydic nature could be detected. The behaviour of phenanthrene with chromyl chloride is therefore similar to that of anthracene, which has already been observed to yield nothing but anthraquinone.

We desire to express our indebtedness to the Committee of the Carnegie Trust for a grant in defrayal of the expenses, and to Mr. A. Gray, F.I.C., for assistance in part of this work.

THE GLASGOW AND WEST OF SCOTLAND TECHNICAL COLLEGE.

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### CVIII.—*Stereoisomeric Glucoses and the Hydrolysis of Glucosidic Acetates.*

By EDWARD FRANKLAND ARMSTRONG (Salters' Company's Research Fellow) and PAUL SEIDELIN ARUP.

*The Stereoisomeric  $\alpha$ - and  $\beta$ -Glucoses.*—In a previous communication on the correlation of the stereoisomeric  $\alpha$ - and  $\beta$ -glucoses with the corresponding glucosides (Trans., 1903, 83, 1305), views were put forward

which have since been confirmed by the work of Behrend and Roth (*Annalen*, 1904, 331, 359) and quite recently by that of C. L. Jungius (*Proc. K. Akad. Wetensch. Amsterdam*, 1904, 779) on the isomeric pentacetates of glucose. There can no longer be any doubt that the supposed third ( $\beta$ ) modification of glucose, described by Tanret, is a mixture; and that, in reality, his  $\gamma$ -form is the modification corresponding with the  $\beta$ -glucosides and therefore properly called  $\beta$ -glucose.

Exception has been taken by Lippmann (*Chemie der Zuckerarten*, 3rd edition, p. 1692) to the view that glucose in solution is a mixture of two stereoisomerides in equilibrium, on the ground that such a mixture, containing as it does varying amounts of  $\alpha$ - and  $\beta$ -glucoses, must vary in properties according to the conditions under which the separation takes place. It is obvious that the proportion of the two forms in equilibrium in solution may be affected by factors such as changes in temperature, concentration, nature of the solvent, presence of foreign substances, &c. When separation takes place, however, the product will vary only in cases in which the conditions of deposition are sufficiently varied. In Tanret's experiments, either the entire mass of sugar in solution at the point of equilibrium was caused to separate as a whole, by precipitating with alcohol; or crystallisation was effected at a high temperature. In the latter case, the temperature selected ( $98^{\circ}$ ) by trial happened to be that which gave rise to an equilibrium identical with that secured prior to the precipitation by alcohol; by working under conditions different from those adopted by Tanret it is easy to obtain mixtures differing from his. Above  $98^{\circ}$ , the  $\beta$ -form predominates, at lower temperatures the  $\alpha$ -modification is in excess.

Although Behrend and Roth, Jungius and Lobry de Bruyn, Lowry and we are now all in agreement as to the nature of Tanret's  $\beta$ -glucose and its non-existence as an entity, there is some doubt as to the nature of the product in solution. Lowry, in a recent communication (*Proc.*, 1904, 20, 108), goes so far as to suggest that together with the  $\alpha$ - and  $\beta$ -forms, a saturated solution of glucose in water contains a large proportion of a third form—probably the aldehyde-hydrate. Although, in order to explain the results arrived at by Lobry de Bruyn, it is apparently necessary to admit that this form is present, yet in view of the fact that aldehydic properties are scarcely manifest, it appears highly improbable that more than relatively very small proportions can co-exist with the two  $\gamma$ -oxide or pentaphane forms.\*

*The Isomeric Glucose Pentacetates.*—The opinion was expressed in a former paper (*ibid.*, p. 1310) that the conversion of  $\alpha$ - and  $\beta$ -glucose pentacetates into one another did not involve the rupture

\* In a former paper, having the expression "lactonartig" in mind, I somewhat incorrectly referred to glucose and the glucosides as  $\gamma$ -lactones.—[E. F. A.].

of the  $\gamma$ -oxide ring. Jungius has recently put forward most important evidence on this point, in showing that it is possible to convert one form into the other in the absence of acetic anhydride, merely by adding to the solution of the acetate in chloroform a small amount of sulphur trioxide.\*

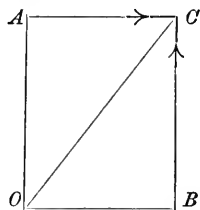
It may be pointed out that in preparing  $\alpha$ -glucose pentacetate, somewhat prolonged boiling of the solution containing zinc chloride is necessary in order to reduce the quantity of the  $\beta$ -acetate to the lowest possible minimum. Prior to the appearance of Behrend and Roth's communication, one of us had attempted to prepare the  $\alpha$ -acetate by instantaneous acetylation of  $\alpha$ -glucose, by adding crystalline  $\alpha$ -glucose to boiling acetic anhydride containing a catalyst,



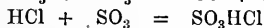
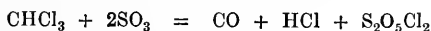
in every case, however, the two acetates were formed.

The phenomena attending the crystallisation of the mixed acetates from a solvent such as alcohol are perhaps more easily followed when expressed graphically.

If  $A$  and  $B$  represent solutions saturated in presence of the  $\alpha$ - and  $\beta$ -pentacetates and  $C$  the solution saturated in presence of both isomerides, the composition of any solution containing both compounds will be represented by a point on the accompanying diagram, unsaturated solutions being indicated by points within the figure, saturated solutions by points along the lines  $AC$  and  $BC$ , supersaturated solutions by points outside  $ACB$ . Solutions represented by points to the left of  $OC$  will deposit only the  $\alpha$ -, whilst those to the right will deposit only  $\beta$ -pentacetate, on removal of the solvent. As one of these forms crystallises out, the relative proportion of the other form present will increase until finally the solution has the composition represented at  $C$ . A mixture of the  $\alpha$ - and  $\beta$ -forms in the proportion in which they are in solution will then separate and continue to do so until the solution dries up: this mixture constitutes Tanret's supposed third isomeride; obviously such a mixture will be unchanged by recrystallisation from the same solvent. The crystallisation of  $\alpha$ - and  $\beta$ -glucoses can be represented in the same manner.—[E. F. A.].



\* It is open to question whether this is the effective agent, as chloroform is decomposed by sulphur trioxide :



(H. E. Armstrong, *Proc. Roy. Soc.*, 1870, 18, 506).

*Hydrolysis of Glucosidic Acetates.*

The experiments described in this section were undertaken in order to extend the data available for the consideration of the influence of configuration on properties in the case of the sugars.

The rate at which hydrolysis takes place, in the case of the pentacetates of glucose and several similar compounds in alcoholic solution, has already been studied by Kreman (*Monatsh.*, 1902, 23, 479); the curves expressing the results which he has put forward are so irregular that it is obvious that the determinations were but roughly approximate and scarcely sufficient to justify the conclusion at which he arrived that the isomeric pentacetates of glucose are hydrolysed at equal rates.

As a matter of fact, it is very difficult to obtain exact results. Hydrolysis is very easily effected and it is necessary, owing to the insolubility of the acetates in water, to dissolve them in alcohol in order to secure admixture with the alkali. In the earlier experiments, the alcoholic solution of the acetate was added to a dilute aqueous solution of alkali, the result being that sufficient heat was developed to raise the temperature of the solution considerably and as the action is half completed within a few minutes, initial errors in the adjustment of the temperature exercise a very considerable influence on the results. This difficulty has been, in part, overcome by using dilute alcohol (33 per cent.) and cooling both the alcoholic solution and the alkali before admixture below the temperature ( $10^{\circ}$ ) at which the interaction was allowed to proceed. Samples were withdrawn at intervals and mixed as quickly as possible with excess of cold acid.

The results obtained with the three pentacetates are recorded in the following table,  $x$  being the amount of alkali neutralised in the successive intervals of time, the values being the means of two concordant experiments;  $K$  the velocity coefficient calculated according to the equation:

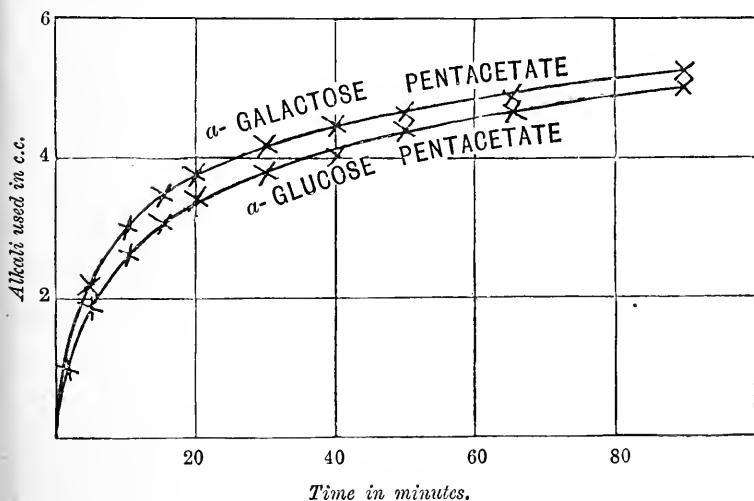
$$K = \frac{1}{(a-b)t} \log \frac{(a-x)b}{(b-x)a},$$

where  $a$  is the concentration of the alkali and  $b$  that of the pentacetate.  $a$ ,  $b$ , and  $x$  are conveniently expressed in terms of  $N/50$  acid. Thus 10 c.c. of the alkali were equivalent to 9.5 c.c. ( $=a$ ) of the acid solution, whilst the acid value of the pentacetate in the same volume was 6.6 ( $=b$ ). In each experiment, 0.3 gram of pentacetate was dissolved in 50 c.c. of alcohol and 100 c.c. of water, cooled to  $8^{\circ}$ ; to this mixture, 100 c.c. of  $N/25$  sodium hydroxide were added.

TABLE I.

Time in minutes.	$\alpha$ -Glucose pent-acetate.		$\beta$ -Glucose pent-acetate.		$\beta$ -Galactose pent-acetate.	
	$x$ .	$K$ .	$x$ .	$K$ .	$x$ .	$K$ .
2	1.0	0.00397	1.0	0.00397	1.25	0.00521
5	1.85	0.00336	1.9	0.00341	2.25	0.00444
10	2.65	0.00279	2.6	0.00271	3.075	0.00354
15	3.125	0.00242	3.15	0.00245	3.5	0.00299
20	3.425	0.00213	3.45	0.00216	3.8	0.00263
30	3.85	0.00177	3.85	0.00177	4.2	0.00217
40	4.1	0.00152	4.15	0.00156	4.5	0.00191
50	4.4	0.00142	4.4	0.00142	4.7	0.00168
65	4.675	0.00127	4.7	0.00129	4.875	0.00146
90	5.1	0.00118	5.05	0.00115	5.3	0.00137
$\infty$	6.6	—	6.6	—	6.6	—

The accuracy attained is best gauged by inspection of the following curve in which the values of  $x$  are plotted against those of  $t$ . As the



experimental points all fall on a smooth curve, the results compare favourably with the irregular values obtained for the three compounds by Kreman.

It will be seen that the values of  $x$  and  $K$  given by the isomeric  $\alpha$ - and  $\beta$ -pentacetates are identical and that  $\beta$ -galactose pentacetate

is hydrolysed considerably faster than the other two esters. Moreover, the value of  $K$  is not constant but decreases as change proceeds, which is an indication that the acetyl groups are not separated at the same rate.

In order to obtain further evidence as to the manner in which the acetyl groups are removed, the experiments were extended to the hydrolysis of the tetracetates of the isomeric  $\alpha$ - and  $\beta$ -methylglucosides and galactosides. In this case, 0.3 gram of acetate having been dissolved in 5 c.c. of alcohol, 100 c.c. of water were added and the solution was then mixed with 100 c.c. of  $N/25$  alkali. No rise in temperature was observed. The results are recorded in the following table, the values of  $x$  being derived from at least two experiments in each case. The value of  $K$  is calculated as before:  $a = 8.7$ ,  $b = 7.9$ .

TABLE II.

<i>T</i> .  Time in minutes.	<i>x</i> .					<i>K</i> .
	$\alpha$ -Methyl- glucoside.	$\alpha$ -Methyl- galactoside.	$\beta$ -Methyl- glucoside.	$\beta$ -Methyl- galactoside.	Mean value.	
2	2.3	2.25	2.2	2.25	2.25	0.00976
4	3.8	3.6	3.6	3.6	3.6	0.01007
6	4.6	4.5	4.4	4.55	4.5	0.01030
10	5.6	5.4	5.35	5.4	5.42	0.00996
15	6.1	5.9	5.7	6.0	6.0	0.00920
20	6.35	6.3	6.1	6.3	6.3	0.00840
30	6.6	6.65	6.5	6.65	6.6	0.00693
40	6.8	6.85	6.8	6.85	6.85	0.00638
50	6.9	6.925	6.9	6.925	6.925	0.0055
60	7.0	7.0	7.0	7.0	7.0	0.0048
$\infty$	7.9	7.9	7.9	7.9	7.9	—

It will be seen that the four compounds are hydrolysed practically at one and the same rate, a fact of special interest when it is remembered that the acetyl groups occupy similar positions in them all. Bearing in mind the difficulty in arriving at exact results, it would seem that hydrolysis takes place at a nearly uniform rate up to the period when change is about three-fourths complete,  $K$  having a fairly constant value; that towards the close, however, change proceeds far less rapidly. It may therefore be supposed that the partially acetylated compounds are more stable than the fully acetylated—a not improbable conclusion.

Inasmuch as Kreman has shown that the behaviour of the oct-acetates of lactose and maltose is similar to that of the glucose pentacetates in that the value of  $K$  decreases with time, the behav-

iour of sucrose octacetate was of peculiar interest. The results obtained are given in the following table; the quantities used were the same as in the case of the tetracetates.

TABLE III.

<i>t.</i>	<i>x.</i>	<i>K.</i>
2 minutes	2.4	0.0106
4     "	3.8	0.0111
6     "	4.4	0.0099
10    "	5.4	0.0098
15    "	6.0	0.0093
20    "	6.2	0.0079
30    "	6.7	0.0075
40    "	7.0	0.0073
50    "	7.2	0.0072
60    "	7.3	0.0068
$\infty$ "	7.9	—

The results appear to indicate that no distinction is to be drawn between the behaviour of the acetyl groups in the sucrose octacetate and those contained in the acetates of the glucoses from which it is derived.

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### CIX.—*The Stereoisomeric Tetramethyl Methylglucosides and Tetramethyl Glucose.*

By THOMAS PURDIE, F.R.S., and JAMES COLQUHOUN IRVINE, Ph.D.,  
D.Sc., Carnegie Fellow.

WE have shown in a former communication (Trans., 1903, 83, 1021) that a dextrorotatory liquid pentamethylated glucose is obtained by methylating  $\alpha$ -methylglucoside with methyl iodide and silver oxide. As the compound had no action on Fehling's solution, and on being hydrolysed gave a tetramethyl glucose which possessed the characteristic properties of a reducing sugar, it was evidently a tetramethyl ether of  $\alpha$ -methylglucoside. By remethylating the tetramethyl glucose with methyl iodide and silver oxide, a lævorotatory, crystalline pentamethyl glucose (m. p. 42—43°) was obtained, but, on account of the

small quantity of material available for examination, it remained uncertain whether this substance was the stereoisomeride of the liquid compound referred to, that is to say, tetramethyl  $\beta$ -methylglucoside, or the pentamethyl glucose of aldehydic structure.

The present research was undertaken with the object of deciding this point, and also of supplementing our previous observations on the optical activity of tetramethyl glucose. This compound, as stated, was found to possess the ordinary properties of an aldose. It was without doubt an etheric derivative of glucose, and its solutions, like those of glucose and aldoses in general, should therefore exhibit multirotation, but this phenomenon, however, could not be detected. As the total lack of this property in a compound of its class seemed very improbable, we thought it necessary to repeat and extend our observations on the rotatory power of the substance.

We find that the crystalline pentamethyl glucose is, as we surmised (*loc. cit.*), tetramethyl  $\beta$ -methylglucoside. The substance crystallises readily on nucleating the crude, syrupy product of the methylation of tetramethyl glucose by the silver oxide method, previous purification by distillation being unnecessary. When this method of alkylation is applied to glucose, the sugar undergoes extensive oxidation, but the methylated glucose resists entirely the oxidising action of the silver oxide. The identification of the crystalline pentamethyl glucose as tetramethyl  $\beta$ -methylglucoside is based on the fact that it behaves like a glucoside towards Fehling's solution, and on its ready hydrolysis by dilute acids, with the production of the same tetramethyl glucose which is obtained by the hydrolysis of the  $\alpha$ -glucoside. The relation of the tetramethyl  $\alpha$ - and  $\beta$ -methylglucosides with respect to rotatory power is the same as that of the corresponding methylglucosides, the  $\alpha$ -compound being dextro-, the  $\beta$ -compound lævo-rotatory; the specific rotations of the former in water were found to be  $+147.4^\circ$  and  $-11.6^\circ$ ,\* those of the latter being  $+157.5^\circ$  and  $-31.85^\circ$  respectively. The means of these values, namely,  $67.9^\circ$  and  $62.83^\circ$ , do not differ very much. The two compounds, like other stereoisomeric glucosides, are also characterised by their behaviour towards emulsin, the  $\beta$ -glucoside being readily hydrolysed by the enzyme, whilst the  $\alpha$ -isomeride is little, if at all, affected even after prolonged heating. Further, we find that in the methylation of tetramethyl glucose by the silver oxide method, the liquid  $\alpha$ -glucoside is produced simultaneously with the crystalline  $\beta$ -compound. We were unable to isolate the former in the pure state, as it retains a large proportion of the latter in solution, and only a partial separation is effected by distillation. The evidence

\* This observation was made in alcoholic solution, but we have reason to believe that the rotatory power in water has nearly the same value.

for the presence of the  $\alpha$ -glucoside in this uncrystallisable mixture is detailed in the experimental part.

The unalkylated hydroxyl group of tetramethyl glucose being in the  $\gamma$ -position, and the compound able, therefore, to assume the tautomeric  $\gamma$ -oxido-forms, methylation should be possible not only by the silver oxide method, but also by Fischer's method (*Ber.*, 1895, 28, 1145) by heating with a dilute solution of hydrogen chloride in methyl alcohol. Tetramethyl glucose is, in fact, methylated by this process more readily than glucose, the action being easily completed at 40°, and here, as in the other method of alkylation, both the isomeric glucosides are produced simultaneously. It is, however, worthy of notice that by the silver oxide process the  $\beta$ -glucoside is produced in notably larger proportion than the  $\alpha$ -glucoside. The former compound was produced in such large excess by this method that it crystallised at once from the syrupy product of the action, whilst in the case of Fischer's method it was obtained after fractional distillation of the product, and then only in small quantity. Polarimetric observations showed that the product of the former process contained at least 70 per cent. of the  $\beta$ -compound, the product of the latter process being 53 per cent. at most. These facts supply a fresh instance of the familiar phenomenon that the alkylation of a tautomeric substance by a method depending on the agency of a silver compound usually differs in its result from other methods of alkylation. The explanation in the present case may be that the  $\beta$ -form of the aldose is of a more acid nature than its isomeride, and more readily gives the unstable silver derivative on the intermediate formation of which the reaction probably depends.

The methylation of glucose by the hydrochloric acid method, like that of tetramethyl glucose by the same method, appears to favour the production of the  $\alpha$ -glucoside (compare Fischer, *loc. cit.*). W. A. van Ekenstein (*Rec. trav. chim.*, 1894, 13, 183—186) found that the glucosides were produced in about equal proportions, but Jungius (*Proc. K. Acad. Wetensch. Amsterdam*, 1903, 6, 99) states that the mixture of methylglucosides obtained by the action of methyl alcohol containing hydrogen chloride on either glucoside contains 77 per cent. of the  $\alpha$ -form. The tetramethyl methylglucosides, however, are not so readily interconvertible. On heating the  $\alpha$ -compound at 40° for 60 hours in methyl alcohol containing 0.25 per cent. of hydrogen chloride under conditions which suffice for the formation of the glucosides from tetramethyl glucose, no fall of rotatory power was observed, and the conversion into the  $\beta$ -compound, therefore, did not occur.

The tetramethyl methylglucosides show a marked difference in their rates of hydrolysis by dilute hydrochloric acid. Parallel experiments,

in which the progress of the action was ascertained by polarimetric observations, showed that 92 per cent. of the  $\beta$ -glucoside, but only 74 per cent. of the  $\alpha$ -compound, was hydrolysed in one hour. The rotatory power of tetramethyl glucose is intermediate with those of the glucosides. As the  $\beta$ -glucoside hydrolyses more rapidly than the  $\alpha$ -isomeride, it follows that, during the hydrolysis of a mixture of the two isomerides such as was obtained in the methylation of the aldose, the rotatory power should at first rise above the value for the hydrolysis product, tetramethyl glucose, and finally fall to the value of this compound; this was found to be the case. Tetramethyl  $\beta$ -methylgalactoside, as shown in the succeeding paper, is also more rapidly hydrolysed than the  $\alpha$ -isomeride.

### *Multirotation of Tetramethyl Glucose.*

As already mentioned, we detected no distinct signs of multirotation in the course of our previous observations on the rotatory power of tetramethyl glucose. On closer examination, we find that the compound does possess the property in question, and that the phenomena exhibited are in every way comparable with those presented by glucose and other reducing sugars. The substance is capable of assuming three forms corresponding closely in their mutual relations with the three forms of glucose first recognised by Tanret, and designated by him  $\alpha$ -,  $\beta$ -, and  $\gamma$ -glucoses.

Of the various theories advanced in explanation of the phenomena of multirotation, as displayed in the sugar group, that of Lowry (*Trans.*, 1899, 75, 213), which attributes the rise or fall of rotatory power to reversible isomeric change, is best in agreement with experimental fact. According to Lowry, Tanret's  $\alpha$ - and  $\gamma$ -forms are dynamic isomerides, and the  $\beta$ -form, which is stable in solution, is a mixture of these in equilibrium. It is only recently, however, that definite evidence has been obtained regarding the structure of the isodynamic forms concerned in the phenomena, which makes it possible to formulate the theory more precisely. Fischer's opinion (*Ber.*, 1893, 26, 2403) that the isomerism of the  $\alpha$ - and  $\beta$ -glucosides and allied series of derivatives is stereochemical and that the compounds have the constitution of  $\gamma$ -oxides may now be accepted as finally established. E. F. Armstrong (*Trans.*, 1903, 83, 1306) has given an excellent summary of the evidence which supports the view, and to this may be added the experimental evidence for the  $\gamma$ -oxido-structure furnished by us in the study of the tetramethyl methylglucosides (*Trans.*, 1903, 83, 1027). If, as is generally supposed, the lactones of aldonic acids are  $\gamma$ -lactones, then tetramethyl gluconolactone is a  $\gamma$ -lactone, and from this it follows necessarily that tetramethyl

methylglucoside and the parent methylglucoside also possess the  $\gamma$ -oxygen linking.

Armstrong's experiments on the hydrolysis of  $\alpha$ - and  $\beta$ -methylglucosides (*loc. cit.*) show conclusively that the products of the action are Tanret's  $\alpha$ - and  $\gamma$ -glucoses respectively, and furnish strong evidence for the view that these forms of the sugar have the glucosidic structure and bear the same stereoisomeric relation to each other as the corresponding glucosides. They are therefore more appropriately named  $\alpha$ - and  $\beta$ -glucoses, and, according to Lowry, it is the establishment of equilibrium by reversible isomeric change between these labile forms which occasions the phenomena of multirotation. The results of Armstrong's hydrolytic experiments have quite recently found happy confirmation in evidence of a synthetical kind furnished by Behrend and Roth (*Annalen*, 1904, 331, 359), which correlates the isodynamic  $\alpha$ - and  $\beta$ -glucoses with the  $\alpha$ - and  $\beta$ -penta-acetates. On acetylating glucose in pyridine solution at 0°, they find that  $\alpha$ -glucose yields the  $\alpha$ -penta-acetate in preponderating quantity, whilst the glucose of permanent rotatory power gives a mixture of the acetates from which the less soluble  $\beta$ -penta-acetate alone could be isolated. The yield of this compound was less than that of the  $\alpha$ -isomeride in the previous experiment, and the conclusion is drawn that the glucose of permanent rotatory power is probably a mixture of the  $\alpha$ - and  $\beta$ -forms.

The reversible change,  $\alpha$ -glucose  $\rightleftharpoons$   $\beta$ -glucose, implies an interchange of the positions of attachment of hydrogen and hydroxyl radicles, and as the view prevails that this cannot occur directly, the interchange has been supposed to be brought about by the breaking of the oxide ring and the subsequent formation of the aldehyde or its hydrate. It is quite possible that the aldehyde plays a part in the establishment of the equilibrium, but the presence of its hydrate as an agent in the process is precluded by the fact recorded below, that anhydrous tetramethyl glucose exhibits all the phenomena of multirotation in organic solvents. Another explanation of the mechanism of the reversible isomeric change in question, advanced by E. F. Armstrong (*loc. cit.*), seems also to be excluded for the same reason.

In describing our observations on the multirotation of tetramethyl glucose, we adopt Lowry's theory provisionally, and assume therefore that the modification of the sugar, which shows a permanent rotatory power, is an equilibrium mixture of the oxide  $\alpha$ - and  $\beta$ -forms (Tanret's  $\alpha$ - and  $\gamma$ -forms).

Pure tetramethyl  $\alpha$ -glucose was obtained from the crude product of the hydrolysis of the  $\alpha$ -glucoside by repeated crystallisation from light petroleum containing a very little ether. The product, after one crystallisation from this solvent, is white and crystalline and presents

all the appearance of a homogeneous substance. Its low and indefinite melting point ( $76-80^{\circ}$ ) and its low initial rotatory power ( $90.6^{\circ}$ ) indicate, however, that it is a mixture in varying proportions of the  $\alpha$ - and  $\beta$ -forms. With repeated crystallisation, the melting point gradually rises, and finally becomes constant at  $88-89^{\circ}$ . The initial specific rotatory power in aqueous solution also rises, as the  $\beta$ -form is eliminated, until it attains the value  $+100.8^{\circ}$ , which is therefore regarded as the specific rotatory power of the  $\alpha$ -isomeride; when this solution is allowed to remain, the rotatory power gradually falls, until after 24 hours it reaches the permanent value  $+83.3^{\circ}$ . The equilibrium mixture of  $\alpha$ - and  $\beta$ -forms, now contained in the solution, can be obtained in the crystalline state, with but little alteration in the proportion of the constituents, by evaporation on a water-bath. Prolonged heating of the residual syrup must be avoided, as this transforms the  $\alpha$ - into the  $\beta$ -form, and the final drying is conducted under diminished pressure at the ordinary temperature until a constant weight is recorded. The melting point of the substance so obtained is no longer that of the pure  $\alpha$ -form, but is again low and indefinite ( $75-80^{\circ}$ ), and when redissolved in water the initial rotation is only slightly higher than the permanent value already quoted, which is soon reached. By repeated crystallisation from light petroleum, the pure  $\alpha$ -form is again obtained. The production of the pure  $\alpha$ -form from the mixture by crystallisation is apparently due to the transformation of the  $\beta$ - into the  $\alpha$ -form, and not merely to its elimination from the mixture by solution. This is shown by the fact that in purifying the original crude compound, whilst the first crystallisation certainly removes a little syrupy matter, in subsequent recrystallisations, although the indefinite melting point and low rotatory power may still betray the presence of the  $\beta$ -form, the mother liquors contain only traces of dissolved matter.

Tetramethyl  $\beta$ -glucose, or more correctly a mixture of this with the  $\alpha$ -form, containing a larger proportion of the former than exists in the equilibrium-mixture, is produced when the  $\alpha$ -form or this mixture is heated for some time above the melting point and then quickly cooled (compare Lowry, *Proc.*, 1904, 20, 108). A crystalline specimen prepared in this way showed in aqueous solution initially the specific rotation  $+73.1^{\circ}$ , which gradually rose, until after 18 hours it reached  $+83.1^{\circ}$ , this being practically the same permanent value as that attained by solutions of the  $\alpha$ -form.

Our previous failure in detecting the multirotation of tetramethyl glucose is no doubt attributable to the specimens examined having been distilled and afterwards crystallised only once or twice from light petroleum. The distillation increases the quantity of the  $\beta$ -form, and the subsequent crystallisation was probably only sufficient to

reduce this to the proportion contained in the stable mixture which shows no multirotation.

Excepting Behrend and Roth's recent observations (*loc. cit.*) on pyridine solutions of glucose, the investigation of the rotatory powers of sugars has been hitherto unavoidably confined to aqueous or alcoholic solutions. Owing, however, to the extreme solubility of tetramethyl glucose, we have been able to examine its rotatory power not only in alcohol, but also in non-ionising solvents such as benzene and carbon tetrachloride. Multirotation occurs in each of these solvents, and the changes of rotatory power are in every case in the same sense as in water, the  $\alpha$ -glucose showing a fall, the  $\beta$ -glucose, prepared as above, a rise of dextrorotation to a permanent value; the range of the change is also much the same as in water, but the rate is much slower. The observations made in these solvents dispose of all the theories of multirotation which are based on the supposed formation of hydrates or compounds of the acetal class. They also show that ionisation is not essential to its occurrence. The addition of a trace of alcoholic ammonia hastens the change greatly, but our experiments do not suffice to decide whether it ceases to occur in the entire absence of catalytic impurities (compare Lowry, *Trans.*, 1903, 83, 1320).

The rotatory power of ordinary glucose varies greatly according as the solvent is water, methyl alcohol, or pyridine. It is worthy of note that, in the case of tetramethyl glucose, the permanent rotation in alcohol, benzene, toluene, and carbon tetrachloride is approximately the same as in water, and that even the initial rotations in the different solvents do not differ much. The following permanent rotations were found in the solvents mentioned: water,  $+83.3^\circ$ ; ethyl alcohol,  $83.1^\circ$ ; benzene,  $84.6^\circ$ ; toluene,  $84.1^\circ$ ; carbon tetrachloride,  $81.6^\circ$ . The specific rotation of the  $\alpha$ -form in benzene ( $111.1^\circ$ ) is somewhat higher than that found in water ( $100.8^\circ$ ), but the real difference is less than these numbers indicate, as the rotatory power of the aqueous solution must undergo a fall of several degrees before the observation can be made. The initial specific rotation of the mixture containing an excess of the  $\beta$ -form, obtained by heating the substance at  $115-120^\circ$ , was  $73.1^\circ$  in water,  $73.5^\circ$  in ethyl alcohol, and  $76.3^\circ$  in benzene. It may be concluded, therefore, that the nature of the solvent has only a slight effect on the permanent state of equilibrium of the isodynamic forms in the solvents mentioned. This result is at variance with the well-known fact that the nature of the solvent has, in general, a marked effect on the composition of the equilibrium-mixtures of dynamic isomerides.

The similarity in the values of the permanent specific rotations in water and in benzene are all the more striking considering that the substance has the normal molecular weight in the former solvent, and

consists of associated double molecules in the latter. Molecular association appears in fact to have no connection with rotatory power (compare Patterson, *Trans.*, 1901, 79, 184; 1902, 81, 1111; also *Trans.*, 1901, 79, 978).

When glucose is crystallised from moderately concentrated solutions in water or alcohol, it is the  $\alpha$ -form which is deposited. Similarly, when tetramethyl glucose is crystallised from light petroleum, in which the substance is not very soluble, it separates in the  $\alpha$ -form. When, on the other hand, it is quickly recovered by evaporation under diminished pressure at the ordinary temperature from solution in a solvent such as benzene, which can be almost entirely removed before crystallisation sets in, the solid mixture so obtained contains the isodynamic forms in nearly the same proportion as that in which they existed in the solution.

The rotatory power of a solution of the equilibrium mixture, which had been recovered from benzene solution, was found to be much lower in methyl iodide than in the other solvents used, but the observations recorded in the experimental part tend to show that, despite the different rotatory power, the isodynamic forms are here present in the same proportion as in other solutions which have attained the stable state.

#### *Relative Stability of the $\alpha$ - and $\beta$ -forms of Tetramethyl Glucose.*

As tetramethyl  $\alpha$ -glucose melts sharply at  $88-89^\circ$ , it may be concluded that the velocity of the isomeric transformation is slow in the immediate neighbourhood of the melting point, and that the  $\alpha$ -modification is therefore the stable form at this temperature.

It is also the stable form at lower temperatures, as the change  $\beta \rightarrow \alpha$  occurs spontaneously in the solid state. This was proved by the following experiments. A dry, crystalline specimen of the mixture of the two forms, which exhibits at once the permanent specific rotatory power ( $83.3^\circ$ ), was prepared from an aqueous solution by the method already described, and was heated in a stoppered tube for 50 hours at  $50-60^\circ$ , a temperature about  $15^\circ$  short of the melting point. After this treatment, a 4 per cent. aqueous solution of the substance showed initially the specific rotation  $+94.7^\circ$ , falling in 12 hours to  $84.8^\circ$ , approximately the permanent value. A portion of the  $\beta$ -form originally present, therefore, had passed while in the solid state into the  $\alpha$ -form. The same transformation takes place at the ordinary temperature. A crystalline mixture containing the  $\beta$ -form in greater proportion than it exists in the equilibrium mixture in solution was prepared, as already indicated, by melting the  $\alpha$ -modification (m. p.  $87-88^\circ$ ) and keeping it for two hours in the fused state at  $120^\circ$ . The solidified

product now melted indefinitely at a temperature ( $51-56^{\circ}$ ) still lower than the melting point of the equilibrium-mixture, and a 5 per cent. solution of it in benzene gave the initial specific rotation as  $76.3^{\circ}$ . A large proportion of the  $\alpha$ -form had therefore been converted by the fusion into the  $\beta$ -form. The remaining portion of this specimen was kept in a stoppered tube at the ordinary temperature for 12 days. The melting point of the substance was now found to have risen to about  $77^{\circ}$ , and in a 4 per cent. benzene solution it showed the initial specific rotation  $87.6^{\circ}$ . So much of the  $\beta$ -form had passed spontaneously in the solid state into the  $\alpha$ -form, that the proportion of the latter now present exceeded the proportion which exists in the mixture of permanent rotatory power. This was confirmed by adding a trace of alcoholic ammonia and letting the solution remain some time, after which the specific rotation was found to have fallen to  $83.4^{\circ}$ .

At temperatures below the melting point, therefore, the non-reversible change  $\beta \rightarrow \alpha$  occurs. The observations on the multirotation of solutions of the fused substance, quoted above, show that at temperatures above the melting point the reverse change sets in, but the final product in this case must necessarily be a mixture of the two forms in equilibrium. A change in the same sense is produced by fusion in the case of glucose, and Tanret (*Bull. Soc. chim.*, 1895, [iii], 13, 733) prepared pure  $\beta$ -glucose (his  $\gamma$ -glucose) by dissolving the mixtures obtained in this manner in water, and then adding alcohol, which caused the deposition of the less soluble  $\beta$ -form. This method is inapplicable in the case of tetramethyl glucose on account of the great solubility of both its forms, and we have not succeeded therefore, in isolating the  $\beta$ -modification in the pure state. Its rotatory power being thus unknown, it is not possible to calculate the composition of mixtures of the two forms.

Tanret examined a series of mixtures of  $\alpha$ - and  $\beta$ -glucoses, obtained by allowing fused  $\alpha$ -glucose to crystallise at definite temperatures between  $75^{\circ}$  and  $97^{\circ}$ , and found that the rotatory powers of the crystalline mixtures decreased from  $84^{\circ}$  to  $39.6^{\circ}$  as the temperature of crystallisation rose. From this it is legitimate to conclude that the proportion of  $\beta$ -glucose in the fused mixture increases with the temperature between the limits given. Our observations on the effect of temperature on the equilibrium of the  $\alpha$ - and  $\beta$ -forms in fused tetramethyl glucose are not extensive enough to enable one to draw exact conclusions, but they indicate that, whilst at temperatures a little higher than the melting point of the  $\alpha$ -form the transformation  $\alpha \rightarrow \beta$  proceeds rapidly, at higher temperatures it nearly ceases. The experiments were made by observing the rotatory powers of the three mixtures obtained from the  $\alpha$ -form by keeping it in a fused state for two hours at  $100^{\circ}$ ,  $120^{\circ}$ , and  $140^{\circ}$  respectively. In each case, the fused mass was solidified by rapid

cooling and the rotatory power examined at once in about a 5 per cent. benzene solution. The initial specific rotations were respectively  $+77.5^\circ$ ,  $76.3^\circ$ , and  $76.6^\circ$ . It seems probable from these observations that the fused substance at  $120^\circ$  consists mainly of the  $\beta$ -form, and that the rotatory power of this form lies not very far below the values quoted; much higher, therefore, than that of  $\beta$ -glucose, which is  $+22.5^\circ$ . If it is admissible to assume that the state of equilibrium of the  $\alpha$ - and  $\beta$ -forms in aqueous solution is the same for glucose as for its tetramethyl derivative, then, calculating from the known rotatory powers of the compounds, the value  $73.5^\circ$  is obtained for tetramethyl  $\beta$ -glucose.

	$\alpha$ -Form.	Equilibrium mixture.	$\beta$ -Form.
Glucose .....	$+106^\circ$	$52.5^\circ$	$22.5^\circ$
Tetramethyl glucose .....	$100.8$	$83.3$	$73.5$

The real specific rotatory power of tetramethyl  $\alpha$ -glucose in water is doubtless some degrees higher than the recorded value,  $100.8^\circ$ , owing to the fall which necessarily occurs before the observation can be taken; this implies that the calculated value for the  $\beta$ -form is somewhat less than the figure quoted. As already stated, the initial specific rotatory power found for an aqueous solution of the fused aldose was  $73.1^\circ$ .

#### EXPERIMENTAL.

##### *Preparation of Tetramethyl $\alpha$ -Methylglucoside and Tetramethyl Glucose.*

Tetramethyl  $\alpha$ -methylglucoside was prepared as before (*loc. cit.*) by the methylation of  $\alpha$ -methylglucoside by means of dry silver oxide and methyl iodide. A partial alkylation was in the first place carried out in methyl alcoholic solution, and after removal of water and alcohol from the product by heating under diminished pressure, the process was completed in methyl iodide solution. Methylglucoside is more soluble in a mixture of methyl alcohol and the methylated product of the action than in the pure alcohol; accordingly it was found that, by adding not only the oxide and iodide but also the glucoside in successive small instalments, the quantity of solvent alcohol could be much reduced. By this modification of the process, some economy in alkylating material was effected, and the yield of completely methylated glucoside was increased to nearly the calculated quantity. Despite the reduced quantity of methyl alcohol present, however, a large part of the alkylating agent was lost owing to the production of dimethyl ether, and a large excess of the mixture therefore had still to be used. Employing 60 grams of Kahlbaum's methylglucoside (1 mol.), 200 c.c. of methyl alcohol, 680 grams of silver oxide (about 9.5 mols.),

and 900 grams of methyl iodide, we obtained, after fractional distillation, 75.5 grams of the tetramethylated glucoside boiling at 145—152° under 13 mm. pressure, of which 62.5 grams passed over at 148—150°. The molecular weight of the compound was determined, as this had not been done previously. The value found in aqueous solution by the cryoscopic method was 223.4, the calculated number being 250. As the determinations of specific rotatory power previously made (*loc. cit.*, pp. 1031, 1039) on different specimens of the substance were not concordant, the observations were repeated on the present preparation with the following results. A 2-dcm. tube was used for the solutions and a 1-dcm. tube for the pure liquid.

	<i>p.</i>	$d_{20}^{20}/4^\circ$ .	$\alpha_D^{20}$ .	$[\alpha]_D^{20}$ .
In ethyl alcohol ...	12.345	0.8201	+ 31.17°	+ 153.9°
In water .....	10.024	1.0131	29.94	147.4
Pure liquid .....		1.1082	171.10	154.4

The specific rotation in alcoholic solution approximates to the highest value previously found, namely, 152.6°; as before, the specific rotation of the pure liquid is nearly the same as that of the alcoholic solution, and a few degrees higher than that of the aqueous solution. The preparation being on a larger scale than formerly, more complete fractionation of the distillate was possible, and we regard the constants now given, including the density of the pure liquid, as more accurate than those recorded in our previous paper.

We have to thank Mr. J. C. Bagot for a determination of the refractive index of the compound. The value at 20°,  $\mu_D = 1.4464$ , approaches closely to that of chloroform.

In our former hydrolyses of the glucoside, the yield of crystalline tetramethyl glucose amounted to only 35 per cent. of the weight of substance taken. If the hydrochloric acid used is too dilute or if the heating is insufficient, the hydrolysis is incomplete, and the unaltered syrupy glucoside prevents crystallisation. If, on the other hand, the hydrolysis is pushed too far, some of the methylated glucose is apparently affected by the prolonged action of the acid, with a similar effect on the yield of crystalline product. By the following modification of the process, the yield of crystallised tetramethyl glucose was raised to 67 per cent. of the weight of glucoside taken. From 7 to 8 grams of glucoside are dissolved in 100 c.c. of about 8 per cent. hydrochloric acid, and the flask containing the solution is heated in boiling water. The progress of the hydrolysis is best followed by frequent polarimetric observations, and the heating is continued just until the observed rotation becomes nearly constant, which occurs in about 3½ hours. The solution, which is usually only slightly coloured, is then neutralised with barium carbonate, filtered, and evaporated to

dryness on a water-bath. The ethereal extract of the residue, after being dried with sodium sulphate and evaporated, gives a syrup which crystallises readily on being nucleated with tetramethyl glucose. A considerable quantity of the syrup, however, fails to crystallise even after a long time, and this has to be removed by spreading the product on a porous tile. The syrup, which is extracted from the tile with ether, gives a further crop of crystals, and the drying on a tile and subsequent extraction of the oil with ether has to be repeated several times in order to obtain the full yield of material. Part of the alkylated sugar may be obtained in a readily crystallisable condition from the neutralised solution of the hydrolysis product by direct extraction with ether in Hagemann's apparatus. Although this method was not found helpful in increasing the yield, it is useful in separating the substance from the gummy by-products which result when the hydrolysis is continued too long.

The melting point of tetramethyl glucose was previously recorded as 81—83°, and in the case of a specimen prepared from cane-sugar as 83—84°. We find that by recrystallisation from light petroleum containing a very little ether the melting point gradually rises, but after five or six crystallisations becomes sharp and constant at 88—89°. This change is due, as explained in the introduction, to the conversion of the  $\alpha$ - into the  $\beta$ -form of the sugar.

Determinations of molecular weight were made in water and in benzene, and the values found were respectively 222 and 475, the calculated value being 236. The substance therefore has the normal molecular weight in water, but is associated in double molecules in benzene.

Tetramethyl glucose differs materially from glucose and other reducing sugars with respect to its cupric-reducing power. The oxidising action of the copper solution is not so vigorous, and as the following quantitative determinations show, it does not proceed so far as in the case of unalkylated sugars. When the substance is heated at 100° with Fehling's solution, very little cuprous oxide is produced, and the solution must be boiled before vigorous reduction occurs. The reducing power is nearly exhausted after 10 minutes, but, despite the presence of unreduced copper in the solution, the latter still remains of a dark brown colour, and on more prolonged boiling continues to deposit minute quantities of cuprous oxide. This behaviour applies also to tetramethyl galactose and is probably characteristic of alkylated sugars in general. The quantitative determination of the reducing power was carried out according to O'Sullivan's method (Trans., 1896, 69, 1692), but, for the reasons explained, the Fehling's solution containing the sugar was boiled for 10 minutes instead of being merely heated in boiling water.

I. 0.3120 gave 0.1280  $\text{Cu}_2\text{O}$ . II. 0.3482 gave 0.1438  $\text{Cu}_2\text{O}$ . Mean : 0.3301 gave 0.1359  $\text{Cu}_2\text{O}$ . This weight of cuprous oxide corresponds with 0.0615 gram of glucose, and the reducing power of tetramethyl glucose is therefore only 18.6 per cent. of that of glucose.

*Tetramethyl  $\beta$ -Methylglucoside.*

*Preparation by the Silver Oxide Process.*—The compound was prepared in the first instance by the method described in our previous paper, namely, by the action of silver oxide and methyl iodide on tetramethyl glucose. The proportion of materials used and the process in other respects were the same as before, but distillation was avoided, as it was found that the liquid product crystallised readily when it was nucleated with the specimen of the substance previously obtained. The  $\beta$ -glucoside was then deposited in delicate needles over an inch in length, and these were separated from adherent liquor by absorbing the latter in a porous tile. The total product from 5 grams of tetramethyl glucose amounted to 5 grams, whilst the crystals (m. p. 30—35°) weighed 1.85 grams. The examination of the uncrystallisable part, which consisted of a mixture of the isomeric glucosides, is described below.

The crystals proved to be so soluble in all the ordinary solvents that it was impossible to recrystallise them in the usual manner; by evaporating an alcoholic solution under diminished pressure, however, until nearly all the solvent was evaporated, the substance solidified as a fine crystalline meal from which the adherent mother liquor was effectually removed by means of a porous tile. The crystals then melted at 40—42°, a result agreeing closely with the melting point formerly recorded, namely, 42—43°. The substance showed only a very faint action on Fehling's solution after boiling for 5 minutes, and this proved to be due to the presence of a trace of some impurity, as after distillation the compound had no reducing action whatever. The *lævorotatory* power of the compound was confirmed, but the specific rotation in about a 5 per cent. alcoholic solution,  $[\alpha]_D^{20} - 11.6^\circ$ , was less than the previously recorded value, namely,  $-13.99^\circ$ .

The hydrolysis of the  $\beta$ -glucoside by dilute hydrochloric acid was carried out under the same conditions as that of its liquid isomeride, and the product was isolated in the same manner. The solution at the outset contained 1.483 grams of the glucoside in 20 c.c., and the observed rotation in a 2-dcm. tube was  $-1.56^\circ$ . The solution in the course of hydrolysis became quickly *dextrorotatory*, and after 2 hours the observed rotation became constant at  $+11.47^\circ$ . The final observed rotation calculated on the assumption that the whole of the substance used was converted into tetramethyl glucose ( $[\alpha]_D^{20} + 83.3^\circ$ ) should be

11.7°, so that the hydrolysis was complete and was not accompanied by other changes.

The syrup obtained from the hydrolysis solidified at once to a hard, crystalline mass readily recognisable as tetramethyl glucose. The weight of the recrystallised substance was 1.04 grams, equal to 74 per cent. of the calculated yield; its melting point was 87—88°, and its permanent specific rotatory power in aqueous solution ( $c = 4.804$ ) was  $[\alpha]_D^{20} + 82.8^\circ$ . The compound was not further purified, but the constants quoted are in agreement with the values found for the tetramethyl glucose produced by the hydrolysis of the  $\alpha$ -glucoside, namely, 88—89° and  $+83.3^\circ$ .

It was to be expected that in alkylating tetramethyl glucose both the stereoisomeric glucosides would be produced. The uncrystallisable part of the product of alkylation therefore consisted presumably of the liquid  $\alpha$ -glucoside with a considerable proportion of the dissolved  $\beta$ -isomeride, and it was accordingly examined with the object of proving the presence of the former compound. The uncrystallisable syrup in question, when recovered by extraction with ether from the tile in which it was absorbed, weighed 2.76 grams. It was neutral towards litmus and had no action on Fehling's solution until it was hydrolysed; it was therefore of a glucosidic nature.

As the  $\beta$ -glucoside boils some 20° lower than its isomeride, the liquid was distilled with the view of further eliminating the former compound from the mixture. The more volatile fraction, weighing 1 gram (b. p. 120—125° under 7 mm. pressure), deposited a small additional quantity of the crystalline  $\beta$ -glucoside, whilst the rest of the distillate, collected at 125—130°, remained liquid and had the composition of the glucosides. The results of analysis were  $C = 52.53$ ,  $H = 8.75$ , the calculated numbers being 52.80 and 8.80 respectively. The view that we were thus dealing with a mixture of the two isomerides was further confirmed by polarimetric observations, and by the result of a quantitative hydrolysis of the liquid. The specific rotatory powers of the  $\alpha$ - and  $\beta$ -glucosides in alcoholic solution are  $+153.9^\circ$  and  $-11.6^\circ$  respectively; the specific rotatory power of the supposed mixture before distillation was found to be, under similar conditions,  $+72.9^\circ$ , and that of the less volatile fraction obtained from it was  $+81.2^\circ$ . The mixture before distillation and the less volatile fraction obtained from the distillation contained, therefore, about 51 and 56 per cent. of the  $\alpha$ -isomeride respectively. Further separation being found impossible, the mixture was hydrolysed. The hydrolysis was carried out under the same conditions and simultaneously with that of the pure  $\beta$ -glucoside described above, the concentration being nearly the same, namely, 1.498 grams in 20 c.c. The observed rotation became constant after heating for 3 hours, and was then

+5.85° ( $l=1$ ). The rotation, calculated on the assumption that the whole of the original material used was glucosidic and was converted completely by the hydrolysis into tetramethyl glucose, should be 5.89°. The product was isolated, as already described, and was found to be nearly pure tetramethyl glucose. The melting point, 87—88°, the permanent rotatory power in a 5 per cent. aqueous solution,  $[\alpha]_D^{20} + 82.8^\circ$ , and the yield of 1.06 grams were identical with the results of the parallel hydrolysis of the pure  $\beta$ -glucoside. A further proof of the presence of the  $\alpha$ -glucoside in the mixture was furnished by the remarkable rise and final fall of rotatory power which occurred during the progress of the hydrolysis; this is alluded to below in connection with the relative rates of hydrolysis of the two glucosides.

We conclude that the product of the alkylation of tetramethyl glucose by means of silver oxide and methyl iodide is a mixture of the two glucosides, and that if the isomeric pentamethylated aldehyde is produced at all in the reaction, it can only be in small quantity. It is evident, also, that the  $\beta$ -glucoside is produced in this reaction in much larger proportion than the  $\alpha$ -isomeride. The weight of the former obtained in the crystalline state was 1.85 grams; the weight of the uncrystallisable mixture was 2.76 grams, about one-half of which, as already stated, consisted of the  $\beta$ -glucoside. The total product therefore contained 70 per cent. of this compound and 30 per cent. of the  $\alpha$ -glucoside.

*Preparation by Fischer's Process* (Ber., 1895, 28, 1145).—Tetramethyl glucose (4.752 grams) was dissolved in methyl alcohol containing 0.25 per cent. of hydrogen chloride and the solution was made up to 100 c.c. with the same liquid. To convert glucose completely into the methyl glucosides, prolonged heating at 100° is requisite, but previous experiment having shown that a temperature of 40° sufficed in the case of tetramethyl glucose, the solution was maintained at this temperature in a closed flask. As the heating proceeded, the action on Fehling's solution gradually diminished until 15 hours had elapsed, when the action could no longer be detected. Polarimetric observations indicated that both glucosides were produced, but the  $\beta$ -isomeride was not present in the greatly preponderating proportion found in the silver oxide method of preparation, and this was confirmed by further examination of the product. The specific rotatory power of the solution before being heated was +84°, and this gradually diminished with the decreasing action on Fehling's solution. Finally, after 24 hours, when the action was stopped, the specific rotatory power, calculated on the weight of tetramethyl glucoside equivalent to the tetramethyl glucose used, was +66.5°. The rotatory powers of the glucosides have not been examined in methyl alcohol, but on the basis of their constants in ethyl alcohol, namely, +153.9° and -11.6°;

the solution then contained 47 per cent. of the  $\alpha$ - and 53 per cent. of the  $\beta$ -glucoside.

The hydrogen chloride having been removed by means of silver carbonate, the solution was decolorised with animal charcoal and evaporated to dryness. Owing to the larger proportion of the liquid  $\alpha$ -glucoside present, the residual syrup did not deposit  $\beta$ -glucoside on being nucleated, as was the case in the other method of alkylation. On distillation, a fraction weighing 1.26 grams was collected at 126—138° under 12 mm. pressure, and a second, weighing 2.38 grams, at 140—150°. Both fractions were glucosidic, as they had no action on Fehling's solution until hydrolysed; the more volatile fraction deposited the crystalline  $\beta$ -glucoside, which was recognised by its melting point, 38—39°; the less volatile fraction remained liquid. By repeating the fractional distillation, a further small quantity of the crystalline glucoside was obtained, but the total yield of the compound in the crystalline state from 4.752 grams of tetramethyl glucose used amounted to only 1 gram.

The presence of the  $\alpha$ -glucoside in the uncrystallisable liquid was proved by its boiling point, by the increased dextrorotation it showed as the  $\beta$ -compound was removed by distillation, and by the composition of the mixture as determined by analysis. The analytical results were C=52.33, H=8.95, the calculated numbers for the glucosides being 52.80 and 8.80 per cent. Further, the same rise and final fall of rotatory power were observed during the progress of the hydrolysis as in the case of the similar mixture of glucosides produced in the silver oxide method of preparation.

#### *Rate of Hydrolysis of Tetramethyl $\alpha$ - and $\beta$ -Methylglucosides.*

Our experience in preparing tetramethyl glucose from these glucosides showed that whilst the  $\beta$ -compound is easily hydrolysed by dilute hydrochloric acid and gives a good yield of aldose, the action in the case of the  $\alpha$ -compound proceeds much less readily. The latter compound, indeed, appears to resist the action of dilute sulphuric acid entirely; when it was heated in a sealed tube at 120° for 1 hour with 10 per cent. sulphuric acid, the liquid remained colourless and devoid of action on Fehling's solution.

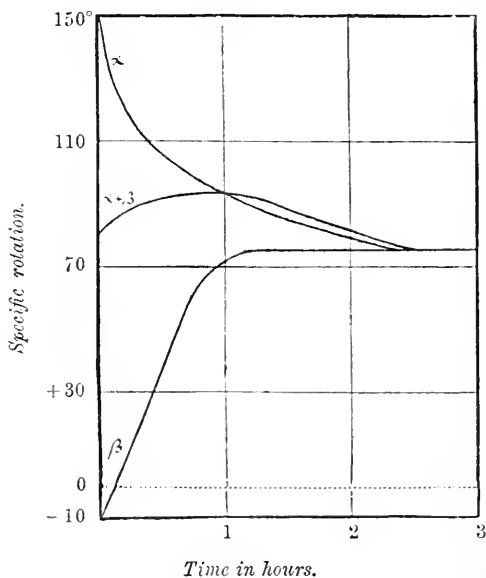
In order to compare the rates of hydrolysis of the glucosides, weighed quantities of each of the pure compounds and of the uncrystallisable mixture obtained in the methylation of tetramethyl glucoside by the silver oxide method were dissolved separately in 8 per cent. aqueous hydrogen chloride, and the solutions made up to definite volumes with this liquid so that the concentrations of the three should be similar. The rotatory powers of the solutions having

been ascertained immediately after their preparation, they were heated in stoppered flasks in boiling water, and polarimetric observations were made at intervals until the hydrolysis was complete. The results, in the form of specific rotations, calculated on the initial concentrations of the glucosides, are quoted below, and are also plotted as curves. The observations show that after one hour 92 per cent. of the  $\beta$ -glucoside was hydrolysed and only 73·8 per cent. of the  $\alpha$ -compound. In the case of the mixture, the rotatory power of the solution could not be determined before heating, owing to its turbidity, and the initial rotatory power quoted is that of the mixture in alcoholic solution, which, for each constituent, does not differ much from the value in water. Owing to the more rapid hydrolysis of the  $\beta$ -glucoside, as pointed out in the introduction, the progress of the action is in this case attended by a rise and subsequent fall of rotation. It will be seen that the specific rotatory powers of the three solutions in the end attain approximately the same value, namely, that of tetramethyl glucose. The final specific rotatory powers, calculated on the concentrations of this compound equivalent to those of the glucosides taken, are  $+79\cdot4^\circ$ ,  $81\cdot9^\circ$ , and  $82\cdot7^\circ$  for the  $\alpha$ -glucoside,  $\beta$ -glucoside, and the mixture respectively; the permanent rotatory power of tetramethyl glucose in pure water is  $83\cdot3^\circ$ .

Time of heating in hours.	$\alpha$ -Glucoside ( $c=7\cdot602$ ).	$\beta$ -Glucoside ( $c=7\cdot415$ ).	Mixture ( $c=7\cdot49$ ).
0	$+149\cdot4^\circ$	$-10\cdot5^\circ$	$+81\cdot2^\circ$
$\frac{1}{2}$	104·5	—	—
1	94·5	$+70\cdot3$	93·6
2	81·3	77·2	83·8
$2\frac{1}{2}$	77·7	77·2	79·3
3	75·2	77·3	78·1
$3\frac{1}{2}$	75·0	—	—

Comparative experiments were also made on the hydrolytic action of emulsin on the glucosides. One gram of tetramethyl  $\beta$ -methylglucoside was dissolved in 10 c.c. of water, and to this was added 0·5 gram of emulsin. The mixture at the outset had no action on Fehling's solution, but after heating at  $37^\circ$  for 4 hours in a thermostat the reducing action was vigorous. The filtered solution was then evaporated to dryness, and the residue was extracted with ether. The liquid left on evaporating the ether reduced Fehling's solution actively, and an alcoholic solution of it showed a dextrorotation. The original glucoside being levorotatory, hydrolysis had therefore been effected. In a comparative experiment with tetramethyl  $\alpha$ -methylglucoside, prepared from Kahlbaum's  $\alpha$ -methylglucoside, hydrolysis also occurred but much more slowly, decided action on Fehling's solution being

detected only after 15 hours' heating. As it was found that Kahlbaum's  $\alpha$ -methylglucoside was similarly affected by emulsin, the experiment was repeated on a specimen of tetramethyl  $\alpha$ -methylglucoside obtained from a specially purified preparation of  $\alpha$ -methylglucoside. In this case, the reducing action after 15 hours' heating was very faint, and only after 24 hours was decided action detected. The slight hydrolysis which occurred in this instance may have been due



to some trace of impurity, and our results therefore on the whole bear out Fischer's experience that susceptibility to the hydrolytic action of emulsin is a characteristic of  $\beta$ -glucosides. We purpose making a more extended study of the action of enzymes on alkylated glucosides.

#### *Multirotation of Tetramethyl Glucose.*

*Aqueous Solutions.*—In order to observe the multirotation of the  $\alpha$ -form, the crude substance was crystallised five times from light petroleum containing a very little ether until the melting point was constant at 88—89°. An aqueous solution was prepared containing 1.5708 grams in 30 c.c. ( $c=5.236$ ), and observations in a 2-dcm. tube were taken at intervals until the rotatory power was constant; the first observation was taken 5 minutes after the solid came in contact with the solvent. The temperature during the first hour was maintained at

20°; later, it was that of the room. Some of the observations are appended.

Time after the preparation of the solution.	$\alpha_D^{20^\circ}$ .	$[\alpha]_D^{20^\circ}$ .
5 minutes	+10.55°	100.8°
15     ,,	10.27	98.1
45     ,,	9.74	93.0
63     ,,	9.44	90.1
28   hours	8.65	82.6
52     ,,	8.72	83.3

The solution of permanent rotatory power was evaporated on a water-bath until on cooling it crystallised and formed a solid mass, which was then completely dried under diminished pressure at the ordinary temperature. An aqueous solution ( $c=5.0016$ ) was quickly prepared and examined at once with the polarimeter. The specific rotatory power was initially only 85.5°, and it became constant at the same value as before, namely, 83.3°. The melting point of the nearly stable mixture of the  $\alpha$ - and  $\beta$ -forms thus obtained was indefinite (75—80°), and considerably lower than that of the pure  $\alpha$ -form. The conversion of the  $\alpha$ - into the  $\beta$ -form in aqueous solution is accelerated in a striking manner by the addition of alkali. A minute drop of very dilute ammonia caused a fall of 5° in the specific rotation in 30 seconds, and the permanent value was reached in 15 minutes. The faintest trace of ammonia on the cover-glass of the polarimeter produces an immediate effect.

With the view of obtaining the  $\beta$ -form of the sugar, or at least a mixture containing a larger proportion of this form than exists in the aqueous solution of permanent rotatory power, a specimen of the latter form in the dry solid state, obtained as described, was distilled under diminished pressure. The distillate, which crystallised at once, was dissolved in water, and the solution ( $c=4.606$ ) was examined for multirotation without delay. The specific rotation initially was now +70.8°, and rose in 2 hours, on a trace of ammonia being added, to 80.7°, at which value it remained constant. The isomeric change  $\alpha \rightarrow \beta$  had therefore been effected by the distillation, and the proportion of the  $\beta$ -form in the mixture had thus been increased; but in solution the reverse transformation was set up, and this proceeded until the mixture had approximately the original composition. As the permanent rotatory power, however, was somewhat short of the limiting value reached by solutions of the pure  $\alpha$ -form, it seemed not unlikely that this might be due to decomposition caused by the distillation, which had of necessity to be conducted rapidly, and the experiment was accordingly repeated in a modified form.

The material used was, as before, the solid mixture of permanent rotatory power, but instead of being distilled it was only kept in a state of fusion for 2 hours at  $115^{\circ}$ , and then quickly cooled. An aqueous solution of the crystalline solid ( $c=5.117$ ,  $l=2$ ) showed the following multirotation:

Time after the preparation of the solution.	$\alpha_D^{20^{\circ}}$ .	$[\alpha]_D^{20^{\circ}}$ .
0	+7.49°	73.1°
1 hour	7.60	74.3
3 hours	8.20	81.1
18 "	8.51	83.1
22 "	8.51	83.1

The final state of equilibrium in solution of the mixture obtained by fusion and sudden cooling is therefore the same as that attained by the  $\alpha$ -form. The change of rotatory power was also in this case accelerated by adding a trace of ammonia.

*Alcoholic Solutions.*—A specimen of tetramethyl glucose, which had been crystallised twice from light petroleum and consisted therefore mainly of the  $\alpha$ -form, was dissolved in ethyl alcohol. The specific rotation of the solution ( $c=4.985$ ) was  $96.3^{\circ}$  initially; this gradually decreased, and, after 48 hours, became constant at  $83.1^{\circ}$ . A portion of the same specimen used in the preceding experiment was kept in the fused state at  $120^{\circ}$  for 2 hours in order to shift the state of equilibrium towards the  $\beta$ -form. The substance was crystallised by rapid cooling, and again examined in alcoholic solution ( $c=4.621$ ). The specific rotation, which was  $73.5^{\circ}$  initially, rose in 72 hours to almost the same limiting value as before, namely,  $82.5^{\circ}$ .

*Benzene Solutions.*—A portion of the same specimen of the pure  $\alpha$ -form, which was used for the observations in aqueous solution, showed initially in benzene solution ( $c=5.248$ ) the specific rotatory power  $+111.1^{\circ}$ , which decreased in 3 hours to  $109.6^{\circ}$ , and 17 hours later to  $104.9^{\circ}$ . The change of rotatory power in this solvent is extremely slow, and the limiting value was not reached in the present instance. That the  $\alpha$ -form had, however, undergone partial conversion was proved by evaporating off the benzene completely under diminished pressure at the ordinary temperature, and observing the rotatory power of the recovered crystalline substance in aqueous solution. The initial specific rotation,  $98.24^{\circ}$ , was less than that of the pure  $\alpha$ -form; the permanent value was approximately the same as in previous experiments. If allowance is made for the fact that the initial rotatory power in benzene is greater than that in water, this experiment shows that a mixture which is still in the

unstable state can be isolated from benzene solution without much change of composition.

In order to compare the permanent rotatory power in benzene with that in water, a fresh solution in this solvent was prepared ( $c=5.075$ ) and observations made at intervals during 4 days in a 2-dcm. tube. Some of these are recorded below :

Time after the preparation of the solution.	$\alpha_D^{20^\circ}$ .	$[\alpha]_D^{20^\circ}$ .
0	+9.86°	97.1°
6 hours	9.52	93.8
24 „	9.36	92.2
60 „	8.67	85.4
75 „	8.59	84.6
100 „	8.59	84.6

The initial rotation recorded here is lower than in the last experiment, as the substance used had been crystallised only twice from light petroleum, and contained therefore a certain proportion of the  $\beta$ -form. The permanent rotatory power does not differ much from that in water, and it may be concluded that the state of equilibrium between the isodynamic forms is nearly the same in the two solvents. To confirm this, a specimen of the equilibrium-mixture was recovered from water and examined in benzene solution, and a specimen of the substance which had been in benzene solution for some days was recovered and examined in water. Multirotation was not observed in either case. The former solution ( $c=5.354$ ) showed the specific rotation  $83.5^\circ$ , the latter ( $c=5.533$ )  $83.1^\circ$ .

The rise of rotatory power due to the conversion of the  $\beta$ - into the  $\alpha$ -form was also observed in benzene solution. A mixture, containing a larger proportion of the  $\beta$ -form than exists in the equilibrium-mixture, was prepared as before, by heating a specimen of the latter mixture in the fused state at  $140^\circ$  for 2 hours. The crystalline substance, obtained by rapid cooling, was examined at once in benzene solution ( $c=7.760$ ); the initial specific rotation was  $+76.6^\circ$ , the permanent value being practically the same as in aqueous solution, namely,  $83.5^\circ$ . The change of rotation in benzene solutions is greatly accelerated by the addition of a trace of alcoholic ammonia.

*Toluene Solution.*—A specimen of the aldose recovered from aqueous solution as previously described, and consisting therefore of the mixture of  $\alpha$ - and  $\beta$ -forms which is stable in water and gives the specific rotation  $83.3^\circ$ , was dissolved in toluene. The initial specific rotation of the solution ( $c=5.150$ ) was  $84.1^\circ$  and no multi-rotation was observed. The state of equilibrium in toluene is therefore nearly the same as in water, alcohol, or benzene.

Experiment having shown that when the substance is distilled or kept in fusion for some time the transformation  $\alpha \rightarrow \beta$  occurs, the toluene solution was subjected to prolonged heating in the expectation that a similar change would occur in the solution; the rate of transformation in the solvent being slow, it was to be expected that on rapid cooling the rotatory power would be found to be temporarily lowered. This, however, was not the case. After heating at  $60^\circ$  for 12 hours and at  $100^\circ$  for 2 hours, the rotatory power remained unchanged. After heating to  $120^\circ$  in a sealed tube, the specific rotation was lowered to  $82.5^\circ$ , but this was not followed by any perceptible rise and was probably due to some slight decomposition. The solution, in fact, had become faintly turbid.

*Solution in Carbon Tetrachloride.*—The aldose used had been kept in the fused state at  $115^\circ$  for 2 hours and was a part of the specimen referred to above, the specific rotation of which in water rose from  $73.1^\circ$  to the permanent value  $83.1^\circ$ . In carbon tetrachloride solution ( $c=4.544$ ) the specific rotation initially was  $76.1^\circ$ ; the value rose in 2 hours to  $78.5^\circ$ , and in 24 hours became permanent at  $81.6^\circ$ . The state of equilibrium therefore does not differ much from that in the other solvents used. The solution after having attained the permanent state was heated at  $50$ – $60^\circ$  for 17 hours, quickly cooled, and examined at once; as in the case of the similar experiment in toluene solution, no alteration in the rotatory power had been produced.

*Solution in Methyl Iodide.*—The crystalline aldose used had been recovered from a solution in benzene, the specific rotatory power of which possessed the permanent value. The substance therefore consisted of the isodynamic mixture which is stable in this and in the other solvents hitherto used. This was confirmed by observing its specific rotatory power in a fresh benzene solution; the value found was  $84.4^\circ$  and no multirotation occurred. A solution of the substance in methyl iodide ( $c=4.880$ ), examined immediately after preparation, showed the specific rotation  $74.8^\circ$ , and this value was permanent. The substance was recovered in the crystalline state by evaporating the methyl iodide under diminished pressure at the ordinary temperature and its specific rotatory power again determined in benzene solution ( $c=4.500$ ), when practically the same initial permanent value as before was found, namely,  $84.6^\circ$ . The rotatory power is therefore much less in methyl iodide than in the other solvents used, but this is not due to the establishment of a different equilibrium by the transformation of  $\alpha$ - into  $\beta$ -form, but to a specific effect of the solvent on the rotatory power such as is commonly observed in the case of homogeneous optically active compounds.

CX.—*The Alkylation of Galactose.*

By JAMES COLQUHOUN IRVINE, Ph.D., D.Sc., Carnegie Fellow, and  
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A METHOD of obtaining alkylated derivatives of sugars in which the hydroxyl groups of the parent substance are partially or completely replaced by methoxyl has been described in a recent paper (Trans., 1903, 83, 1021). The process consists in alkylating a soluble glucoside by means of dry silver oxide and methyl iodide, the final product of this reaction being a completely methylated sugar of glucosidic structure. These compounds on hydrolysis lose only the glucosidic alkyl group, and yield an alkylated aldose or ketose possessing most of the properties of a reducing sugar. Although the method seems to be a general one, the only compounds of this class which so far have been studied in detail are the various alkylated derivatives of glucose. The present paper deals with the preparation and examination of the isomeric tetramethyl  $\alpha$ - and  $\beta$ -methylgalactosides and with the alkylated sugar obtained from these compounds by hydrolysis.

The material used as a starting point was Fischer's  $\alpha$ -methylgalactoside, which was purified as far as possible from the  $\beta$ -form by recrystallisation from ethyl acetate. Alkylation by means of dry silver oxide and methyl iodide was effected in the first place in methyl-alcoholic solution, and finally, when the methylation had proceeded far enough, in methyl iodide. The product of this reaction was tetramethyl  $\alpha$ -methylgalactoside, which boiled at 136–137° under 11 mm. pressure. Like the corresponding alkylated glucoside, this compound is a colourless, refractive liquid, readily soluble in organic solvents. In the pure state, the compound showed a specific rotation of +105.7°, and this agrees approximately with the value given by a 10 per cent. solution in alcohol, which equals +109.9°. In water, however, the rotatory power is much higher, a 10 per cent. solution giving  $[\alpha]_D^{20} +143.4^\circ$ . In this respect a fully alkylated galactoside differs from the isomeric glucoside, the rotation of which is not much affected by solution in alcohol or water. The compound, as was to be expected, displayed no multirotation.

It will be seen that alkylation lowers the dextrorotation of  $\alpha$ -methylgalactoside considerably, but this difference is small compared with the marked increase of rotatory power due to the introduction of the glucosidic methyl group. This is shown by the following numbers :

	Solvent	$[\alpha]_D$
Galactose .....	water	+80.4°
$\alpha$ -Methylgalactoside .....	„	179
Tetramethyl $\alpha$ -methylgalactoside .....	„	143.3

At the same time, as  $\alpha$ -methylgalactoside probably corresponds with the  $\alpha$ -form of galactose, the increase of rotation due to glucosidic methylation is not so great, as  $\alpha$ -galactose possesses a specific rotation of  $+135^\circ$  (*Bull. Soc. chim.*, 1896, 15, 195), but nevertheless the introduction of one methyl group into the glucosidic position has a greater effect than the subsequent methylation of the four remaining hydroxyl groups. The rotation values quoted by us for the alkylated  $\alpha$ -galactoside are perhaps too low, as possibly the substance contained a little of the  $\beta$ -isomeride, derived from the presence of a trace of  $\beta$ -methylgalactoside in the original material. This view was supported by the fact that emulsin effected a feeble although evident hydrolysis of the compound.

The hydrolysis of the alkylated galactoside was carried out by heating with 8 per cent. aqueous hydrochloric acid in boiling water until the rotation of the liquid diminished to a constant value. The product of the reaction was tetramethyl galactose, which was distilled at  $172^\circ$  under 13 mm. pressure. The compound could not be made to crystallise, and our experiments on multirotation were therefore restricted.

When distilled, or after heating for some time at  $130^\circ$ , the sugar behaved like  $\beta$ -galactose, the rotation in water, alcohol, or benzene gradually increasing to constant values. These changes were, however, comparatively small, particularly in the case of the alcoholic solution. Although on the whole comparable to the multirotation displayed by tetramethyl glucose when similarly dissolved, it is worthy of note that the permanent values recorded differ greatly in the three solvents specified, the numbers obtained for the aqueous alcoholic, and benzene solutions being respectively  $+109.5^\circ$ ,  $+62.6^\circ$ , and  $+90.0^\circ$ . On recovering the sugar from its solutions in alcohol or benzene and redissolving in water, only slight multirotation was observed, and the permanent specific rotation of  $+108.8^\circ$  was obtained in each case. It would therefore appear that fusion or distillation converts alkylated galactose partially into the  $\beta$ -form, and in different preparations, although the initial rotations varied somewhat, the final values in aqueous solutions were practically identical. As in the case of the ordinary reducing sugars, the addition of a trace of alkali caused the aqueous or alcoholic solutions to attain a constant rotation almost instantaneously, and a little alcoholic ammonia produced the same effect on the solutions in benzene.

The behaviour of tetramethyl galactose towards the alkylating mixture of silver oxide and methyl iodide is in accordance with the idea that the methylated sugar possesses the  $\gamma$ -oxidic structure. The reaction yielded the tetramethyl  $\alpha$ - and  $\beta$ -methylgalactosides, the latter, a crystalline compound melting at  $44-45^\circ$ , being produced

in much greater quantity than the  $\alpha$ -isomeride. The alkylated  $\beta$ -galactoside closely resembles the corresponding  $\beta$ -glucoside; it is readily crystallised, and in alcoholic solution is lævorotatory with  $[\alpha]_D^{20} - 20.9^\circ$ . In water, however, the substance is dextro-rotatory, having  $[\alpha]_D^{20} + 30.7^\circ$ , and it is thus seen that both the  $\alpha$ - and  $\beta$ -forms show in water a much higher rotation in the dextro-rotatory sense than in alcohol.

The hydrolysis of the  $\beta$ -form proved to be very rapid, as a solution in 8 per cent. aqueous hydrochloric acid attained a constant rotation after 15 minutes' heating in boiling water. The compound was also easily hydrolysed by emulsin.

The tetramethyl  $\alpha$ -methylgalactoside produced in the foregoing alkylation was not isolated in a state of purity, owing to the difficulty in separating it from the dissolved  $\beta$ -form by fractionation. Distillation yielded a liquid of glucosidic nature showing a dextro-rotation in alcohol ( $[\alpha]_D^{20} + 21.5^\circ$ ), and which gave on analysis figures for a fully alkylated methylgalactoside. We therefore conclude that it consists of a mixture of the two forms, and this was confirmed by a study of the hydrolysis. As the  $\beta$ -form is hydrolysed more quickly than the more strongly dextro- $\alpha$ -isomeride, it follows that during the hydrolysis of a mixture of the two forms the rotation should at first increase above the value for the hydrolysis product and afterwards diminish to a constant value. It was found that a solution in 8 per cent. hydrochloric acid of the liquid mixture of the two glucosides obtained in a second preparation showed initially a specific rotation of  $+69.9^\circ$ . During heating, the rotation was taken at intervals of ten minutes, and after two such periods the maximum value of  $+110^\circ$  was recorded. This subsequently diminished to  $+96.1^\circ$ , when the rotation remained constant.

The tetramethyl galactose was also condensed with methyl alcohol in the presence of hydrochloric acid. The product of this reaction was likewise a mixture of the tetramethyl  $\alpha$ - and  $\beta$ -methylgalactosides, but, judging from the rotation in alcohol of the liquid obtained, the  $\alpha$ -form is produced in large excess.

It would therefore appear that the methylation of an alkylated sugar proceeds in a different fashion according as to whether methyl alcohol and hydrochloric acid or a mixture of silver oxide and methyl iodide is used as the condensation agent. In both the preparations described, the sugar used contained presumably an excess of the  $\beta$ -form, but the prolonged heating in solution would transform it into the equilibrium mixture of the  $\alpha$ - and  $\beta$ -varieties. The different result obtained in the two cases may add one more example to the already numerous list of the abnormal reactions of organic silver derivatives.

## EXPERIMENTAL.

The  $\alpha$ -methylgalactoside used in our experiments was prepared by Fischer's method (*Ber.*, 1895, 28, 1154), in which dry galactose is heated at  $100^\circ$  with methyl alcohol containing 0.25 per cent. hydrochloric acid. A slight variation was introduced into the preparation, as, after removal of the free acid, the reaction product was found to crystallise rapidly on nucleation, and in this way a mixture of  $\alpha$ - and  $\beta$ -methylgalactosides amounting to 55 per cent. of the sugar taken was easily obtained. The  $\alpha$ -form was then separated as usual by recrystallisation from ethyl acetate.

The alkylation of the compound was carried out in three stages. In the first place, the methylgalactoside (1 mol.) was dissolved in boiling methyl alcohol containing methyl iodide (10 mols.), and dry silver oxide (5 mols.) gradually added. The reaction started on gently warming the mixture, and after the addition of all the oxide was continued for some hours on a water-bath. The product was extracted with boiling alcohol, and, after removal of the solvent, was freed from water by heating under diminished pressure at  $100^\circ$ . The syrup thus obtained dissolved readily in about its own weight of methyl alcohol, and a second treatment with the same proportion of alkylating mixture was carried out on the solution. An extraction with ether was now made and the product was, as usual, dried at  $100^\circ$  under diminished pressure, a precaution which is necessary in order to ensure good yields. The final treatment was carried out in methyl iodide solution, the same proportions of oxide and iodide being employed. Extraction with ether was repeated and, after removal of the solvent, the product was obtained as a colourless liquid which was distilled under diminished pressure. After fractionation, the pure compound boiled at  $136$ — $137^\circ$  under 11 mm. pressure. The higher fractions, which consisted of incompletely methylated product, were again alkylated as usual, and thus utilised. In different preparations, the total yield of fractionated material was about the same, amounting to 77 per cent. of the methylgalactoside taken.

0.1894 gave 0.3674  $\text{CO}_2$  and 0.1528  $\text{H}_2\text{O}$ .  $\text{C} = 52.90$ ;  $\text{H} = 8.95$ .

0.3480 „ 1.6100  $\text{AgI}$ .  $\text{CH}_3\cdot\text{O} = 61.07$ .

$\text{C}_{11}\text{H}_{22}\text{O}_6$  requires  $\text{C} = 52.80$ ;  $\text{H} = 8.80$ .  $\text{C}_6\text{H}_7\text{O}(\text{O}\cdot\text{CH}_3)_5$  requires  $\text{CH}_3\cdot\text{O} = 62.00$  per cent.

The compound is a fairly mobile, colourless liquid, readily soluble in water and all the usual organic solvents, and is devoid of any action on Fehling's solution until after it has been hydrolysed. Under the ordinary pressure, it distils with but little decomposition at  $260$ — $262^\circ$ .

The following observations were made on the optical activity of the substance :

Solvent.	<i>c.</i>	<i>l.</i>	$\alpha^{20^\circ}$ .	$[\alpha]_D^{20^\circ}$ .
Ethyl alcohol	10.2460	2.	+ 22.54°	+ 109.9°
" "	10.2440	2.	21.19	103.4
Water	10.0180	1.	14.36	143.4

It will thus be seen that a considerable difference exists in the rotation in aqueous and in alcoholic solution. The value in the latter case, however, approximates closely to that obtained for the pure liquid, which gave in a 1-dcm. tube a rotation of +117.10° at 20°. As the sp. gr. is 1.10727 at 20°/4°, the specific rotation of the pure compound becomes +105.7° at 20°.

*Action of Emulsin.*—The action of emulsin on the compound was carried out according to Fischer's method (*Zeit. physiol. Chem.*, 1899, 26, 65), two parts by weight of the galactoside being mixed with one of the enzyme and ten of water ; the mixture was then maintained at 37° for some hours. After eight hours' treatment, the filtered liquid reduced Fehling's solution slightly, but the reducing action did not increase appreciably on continuing the heating for 24 hours. This slight hydrolysis may in all probability be due to the presence of a little  $\beta$ -methylgalactoside in the original material. The result is, however, quoted, as on this assumption the rotations given for the alkylated  $\alpha$ -galactoside are subject to correction.

#### *Tetramethyl Galactose.*

This compound can be prepared by the hydrolysis of either  $\alpha$ - or  $\beta$ -tetramethyl methylgalactoside, and the method followed was substantially the same in each case. A 7.5 per cent. solution of the alkylated galactoside was made in water containing 8 per cent. of hydrochloric acid and heated in boiling water ; the course of the hydrolysis was traced by means of polarimetric observations.

In the case of the  $\alpha$ -isomeride, it was found that ninety minutes' treatment caused the specific rotation (calculated on the weight of alkylated galactoside taken) to diminish from +154° to +96°, and this value remained constant for another hour, although prolonged heating occasioned a slight rise in the activity. The hydrochloric acid was neutralised with barium carbonate, the filtered solution evaporated to dryness, and the residue extracted with ether. After drying the solution over sodium sulphate and removal of the solvent, a colourless syrup remained which was fractionated under diminished pressure. The pure substance boiled steadily at 172° under 13 mm. pressure.

0.2025 gave 0.3774  $\text{CO}_2$  and 0.1576  $\text{H}_2\text{O}$ .  $\text{C} = 50.82$  ;  $\text{H} = 8.64$ .

0.4866 „ 1.9676  $\text{AgI}$ .  $\text{CH}_3\cdot\text{O} = 53.40$ .

$\text{C}_{10}\text{H}_{20}\text{O}_6$  requires  $\text{C} = 50.85$  ;  $\text{H} = 8.47$  per cent.

$\text{C}_6\text{H}_8\text{O}_2(\text{O}\cdot\text{CH}_3)_4$  requires  $\text{CH}_3\cdot\text{O} = 52.54$  per cent.

Unlike the isomeric alkylated glucose, the compound could not be made to crystallise, and was therefore examined in the form of a highly refractive syrupy liquid. It is readily soluble in water, alcohol, ether, or benzene, and dissolves with some difficulty in boiling light petroleum ; from its solution in the last solvent it is deposited on cooling as an oil.

The substance possesses a bitter taste, turns brown when boiled with aqueous caustic soda, reduces Fehling's solution readily on warming, and gives the Molisch reaction with  $\alpha$ -naphthol and sulphuric acid. When dissolved in water, alcohol, or benzene, the compound exhibited multirotation, the permanent values for the three solvents specified being :

	$[\alpha]_D^{20^\circ}$ .
Aqueous solution .....	+ 109.5°
Alcoholic „ .....	62.6
Benzene „ .....	90.0

#### *Multirotation of Tetramethyl Galactose.*

When tetramethyl galactose is freshly distilled or has been heated for some time at  $130^\circ$ , the rotations of solutions in water, alcohol, or benzene are much lower than the foregoing permanent values. Thus, a 3 per cent. aqueous solution of the distilled sugar gave at once a specific rotation of  $+102.2^\circ$ ; this value gradually rose and in eight hours became constant at  $+109.5^\circ$ , the difference in the actual observation amounting to half a degree. The addition of a trace of alkali to the solution was found to accelerate the change greatly without appreciably affecting the end value. In benzene, the change is more marked, but is of course much slower. A freshly-prepared solution of material which had been heated for two hours at  $130^\circ$  gave  $[\alpha]_D^{20^\circ} +73.0^\circ$ , and this, after two days, increased to the constant value of  $+90.0^\circ$ .

The end value reached in alcoholic solution differs considerably from that found in water or in benzene. Thus a 6.09 per cent. solution of the distilled sugar gave in a 2-dcm. tube a rotation of  $+7.10^\circ$ , from which  $[\alpha]_D^{20^\circ} = +58.3^\circ$ . This gradually increased, until at the end of two days the constant rotation of  $+7.63^\circ$  was reached, the specific rotation having therefore increased to  $+62.6^\circ$ . As a control experiment, the sugar was recovered from its solution, redissolved in water, and the rotation redetermined in this solvent.

For  $c = 9.468$ ,  $l = 1$ ,  $\alpha^{20} = +9.94$ ,  $[\alpha]_D^{20} = +104.9^\circ$ .

On adding a drop of dilute ammonia, the rotation at once increased to  $+10.30^\circ$ , for which  $[\alpha]_D^{20}$  is  $+108.8^\circ$ , a number which agrees closely with the permanent value ( $109.5^\circ$ ) already recorded for an aqueous solution.

### *Reducing Power of Tetramethyl Galactose.*

The quantitative action of the compound on Fehling's solution was determined by O'Sullivan's gravimetric method (Trans., 1896, 69, 1691). At the same time, it is doubtful whether the process can be applied accurately to alkylated sugars, for, whereas these substances undergo decomposition with the alkali present, the resulting brown liquid is oxidised by the copper solution only slowly and at the boiling point. Constant results were, however, obtained when the conditions as to concentration and time of boiling were kept strictly uniform in the different determinations. After preliminary experiments, the following proportions were adopted: 50 c.c. of the sugar solution containing 0.2947 gram of substance were raised to boiling and mixed with 18 c.c. of standard Fehling's solution diluted with 18 c.c. of water and maintained at the boiling point. Although cuprous oxide was immediately deposited, the reduction was not complete until after about 10 minutes' boiling. After this treatment, the filtered solution, which contained an excess of copper, became dark brown, and on prolonged boiling only deposited a trace of cuprous oxide. The precipitate was collected in a Soxhlet filtering tube and weighed as  $\text{Cu}_2\text{O}$ . In this experiment, 0.1312 gram was obtained, and this represents the average result.

It will thus be seen that the reducing power of tetramethyl galactose is much lower than that of the parent sugar, and amounts to only about 22 per cent. of that of glucose.

### *Action of Phenylhydrazine on Methylated Galactose.*

On mixing molecular proportions of the alkylated sugar and phenylhydrazine dissolved in dilute acetic acid, a clear solution was obtained which, when left for some days in the dark, deposited a light yellow oil. Examination of the aqueous layer showed that practically all the base had reacted. The separated oil, after washing with cold dilute acetic acid, had no action on Fehling's solution; it nevertheless contained both the sugar and hydrazine residues, as a qualitative examination showed that both nitrogen and methoxyl were present. When hydrolysed with dilute hydrochloric acid, the products reduced Fehling's solution readily in the cold. As the substance could not be

obtained crystalline, no analyses were attempted, but from its production and reactions the compound is undoubtedly a hydrazone.

*Alkylation of Tetramethyl Galactose.*

The addition of silver oxide ( $5\frac{1}{2}$  mols.) to a solution of the sugar (1 mol.) in methyl iodide (11 mols.) occasioned a feeble reaction which was continued for eight hours on a water-bath. The product was extracted with boiling ether and, after drying the solution over sodium sulphate, the solvent was removed by evaporation. The residual oil had no action on Fehling's solution until hydrolysed, and hence possessed the glucosidic structure. After a few hours, the liquid crystallised to a mass of slender needles which were separated by spreading on a porous plate.

The solid product of the reaction proved to be very soluble in water and organic solvents, and was recrystallised with some difficulty from a concentrated solution in light petroleum. The crystals then melted sharply at  $44-45^\circ$ , and behaved like a glucoside towards Fehling's solution. A 5.03 per cent. solution in ethyl alcohol with  $l = 1$  gave a rotation of  $-1.05^\circ$  at  $20^\circ$ , hence  $[\alpha]_D^{20} = -20.9^\circ$ , and this value remained constant. On the other hand, the rotation in water is dextrorotatory, as a 4.168 per cent. aqueous solution gave  $l = 1$ ,  $\alpha^{20} + 1.28^\circ$ , from which  $[\alpha]_D^{20}$  is  $+30.7^\circ$ . It is thus seen that in the case of both the isomeric alkylated  $\alpha$ - and  $\beta$ -methyl galactosides the rotation in water is much higher in the dextrorotatory sense than in alcohol. On recovering the  $\beta$ -form from the foregoing aqueous solution and redissolving in alcohol, the levorotation in this solvent was confirmed.

The specimen for analysis was dried under diminished pressure.

0.1720 gave 0.3332  $\text{CO}_2$  and 0.1370  $\text{H}_2\text{O}$ .  $\text{C} = 52.72$ ;  $\text{H} = 8.85$ .

0.1869 „ 0.8898  $\text{AgI}$ .  $\text{CH}_3\cdot\text{O} = 62.85$ .

$\text{C}_{11}\text{H}_{22}\text{O}_6$  requires  $\text{C} = 52.80$ ;  $\text{H} = 8.80$  per cent.

$\text{C}_6\text{H}_7\text{O}(\text{O}\cdot\text{CH}_3)_5$  requires  $\text{CH}_3\cdot\text{O} = 62.0$  per cent.

The compound, which has therefore the composition of tetramethyl methylgalactoside, represents the  $\beta$ -isomeride, and in accordance with this view the substance was found to be hydrolysed very readily with emulsin. On heating in boiling water with 8 per cent. hydrochloric acid for 15 minutes, the compound was completely hydrolysed with the production of tetramethyl galactose. As in this case also the alkylated sugar failed to crystallise, its identity was established by analysis.

The liquid product of the alkylation was extracted from the tile by means of ether. A second crop of the methylated  $\beta$ -galactoside slowly crystallised, and hence the processes of separation on a tile and extraction with ether were repeated. The liquid thus obtained would

not crystallise, and distilled at 135—140° under 11 mm. pressure. The distillate behaved like a glucoside towards Fehling's solution, and showed a dextrorotation in alcohol.

For  $c = 7.647$ ,  $l = 1$ ,  $\alpha^{20} + 1.65^\circ$ , from which  $[\alpha]_D^{20}$  is  $+21.5^\circ$ .

0.2690 gave 0.5200  $\text{CO}_2$  and 0.2135  $\text{H}_2\text{O}$ .  $\text{C} = 52.72$ ;  $\text{H} = 8.82$ .

0.2771 „ 1.2866  $\text{AgI}$ .  $\text{CH}_3 \cdot \text{O} = 61.30$ .

$\text{C}_{11}\text{H}_{22}\text{O}_6$  requires  $\text{C} = 52.80$ ;  $\text{H} = 8.80$ .

$\text{C}_6\text{H}_7\text{O}(\text{O} \cdot \text{CH}_3)_5$  requires  $\text{CH}_3 \cdot \text{O} = 62.00$  per cent.

The analysis and behaviour towards Fehling's solution show that the liquid product of the alkylation has also the composition of a tetramethyl methylgalactoside, and from the low dextrorotation in alcohol we conclude that it consists of a mixture of the  $\alpha$ - and  $\beta$ -isomerides which cannot be completely separated by fractionation.

The yield of the crystalline  $\beta$ -galactoside from the reaction amounted to 60 per cent. of the sugar taken, whilst only 25 per cent. of distilled oil was obtained, and that, judging from its rotation in alcohol, still contained some of the  $\beta$ -form.

*Comparison of the Rates of Hydrolysis of the Isomeric Tetramethyl  $\alpha$ - and  $\beta$ -Methylgalactosides.*

In the case of the corresponding isomeric alkylated glucosides, a considerable difference exists in the rate of hydrolysis of the two compounds, the  $\beta$ -form decomposing much more readily than the  $\alpha$ -modification, and a similar relationship was found to hold for the alkylated galactosides. Known weights of the two compounds were dissolved in water and hydrochloric acid added, after which the solutions were diluted to standard volume so as to give 8 per cent. acid solutions. The rotation of each was taken at once and afterwards at definite time intervals during the reaction, which was carried out by heating in boiling water. The following table shows the change of specific rotation in either case, the values being calculated on the weight of galactoside taken.

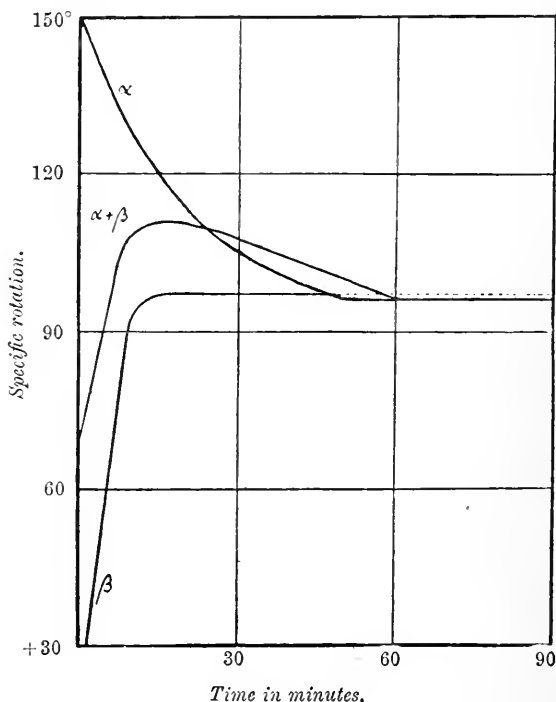
Time from the start.	$\alpha$ -Form. [ $\alpha$ ] <sub>D</sub> .	$\beta$ -Form. [ $\alpha$ ] <sub>D</sub> .
0	+ 154°	+ 30.7°
15 mins.	—	98.6
30 „	104.8	98.6
60 „	97.0	
90 „	96.0	
120 „	96.1	

Representing the above results graphically, it is seen that the curve for the hydrolysis of the  $\beta$ -form becomes horizontal much sooner than that of the  $\alpha$ -isomeride.

As explained in the introduction, the curve for the hydrolysis of a mixture of the  $\alpha$ - and  $\beta$ -forms ought to show a rise and fall, and an experiment made with the liquid product of the alkylation of tetramethyl galactose by means of silver oxide and methyl iodide showed this to be the case. The conditions as to concentration and strength of acid used were the same as in the foregoing hydrolyses, and the following numbers show the change in activity.

Time of heating.	$[\alpha]_D^{20^\circ}$ calculated on the weight of galactoside taken.
0	+ 69.9°
10 mins.	108
20 „	110
30 „	109
60 „	96.1
90 „	constant

The above figures are also included in the diagram.



*Condensation of Tetramethyl Galactose with Methyl Alcohol.*

Freshly distilled tetramethyl galactose was dissolved in twenty times its weight of methyl alcohol containing 0.25 per cent. hydrochloric acid, and the solution heated in a thermostat at 60° for twenty hours. The liquid became straw-yellow and the action on Fehling's solution rapidly disappeared. The rotation of the reaction mixture at first increased, and then decreased slightly, and heating was continued until a constant activity was recorded. The hydrochloric acid was removed by treatment with barium carbonate, the filtered solution evaporated to dryness, and the residue extracted with ether. After removing the ether, a yellow, mobile liquid remained which was fractionated under diminished pressure. About 90 per cent. of the weight of sugar taken was obtained boiling at 135—140° under 14 mm. pressure. As nucleation with the alkylated  $\beta$ -galactoside failed to promote crystallisation, it was evident that this compound had not been produced in large excess in the reaction, a fact which was confirmed by the rotation of the distilled liquid. The syrup behaved like a glucoside towards Fehling's solution.

0.1530 gave 0.2963  $\text{CO}_2$  and 0.1246  $\text{H}_2\text{O}$ .  $\text{C} = 52.81$ ;  $\text{H} = 9.02$ .

0.1817 „ 0.8280  $\text{AgI}$ .  $\text{CH}_3\cdot\text{O} = 60.2$

$\text{C}_{11}\text{H}_{22}\text{O}_6$  requires  $\text{C} = 52.80$ ;  $\text{H} = 8.80$ .

$\text{C}_6\text{H}_7\text{O}(\text{O}\cdot\text{CH}_3)_5$  requires  $\text{CH}_3\cdot\text{O} = 62.0$  per cent.

The product therefore possesses the composition of tetramethyl methylgalactoside and consists of a mixture of the  $\alpha$ - and  $\beta$ -forms, as was shown from the rotations in alcohol and water. In alcohol,  $c = 9.327$ ,  $l = 2$ ,  $\alpha^{20^\circ} = +17.19^\circ$ , from which  $[\alpha]_D^{20^\circ}$  is  $+92.1^\circ$ . In water, the specific rotation was  $+119.5^\circ$ , and these numbers indicate that the mixture consists of about 80 per cent. of the  $\alpha$ - and 20 per cent. of the  $\beta$ -form.

We intend to continue our investigations on methylated galactose, particularly with the view of applying our results to the alkylation of lactose.

In conclusion, we desire to tender our thanks to Professor Purdie for his kindly interest and valuable advice in the work, and also to the Executive Committee of the Carnegie Trust for defraying the entire expense of the investigation.

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CXI.—*Ionisation and Chemical Combination.*

By JAMES WALLACE WALKER.

THERE is a sentence in Ostwald's *Lehrbuch*, 1893, II, 1, 786, which runs: "Eine sehr grosse Zahl chemischer Vorgänge beruht auf der Bildung von Ionen aus neutralen Körpern and umgekehrt." This statement is the key to the development of a very large portion of the views which have been expressed regarding the mechanism of chemical change during the past decade. From a brief summary of these opinions, as given by Walden (*Zeit. physikal. Chem.*, 1903, 43, 394), it is evident that the tendency at present is to throw more and more stress on the rôle played by the ions in chemical change. We find reactions of all kinds ascribed to them, whether the recognised methods of demonstrating their existence indicate their presence or not, and possibly the majority of chemists will now subscribe to the statement of Arrhenius (*Lehrbuch der Elektrochemie*, 1901, 171): "Man kann sogar so weit gehen, zu behaupten, dass nur Ionen chemisch reagiren können." That the ionised condition—whatever views may be held regarding its nature—is one in which different kinds of matter are peculiarly liable to mutual interaction is sufficiently manifest, and, although the degree of ionisation of a liquid generally diminishes to an almost infinitesimal amount when the liquid reaches a high degree of purity, the contention that there are still sufficient ions present to account for its manifestations of chemical change when brought into contact with another substance is one which it is by no means easy to combat, however unsatisfactory it may appear when applied to individual cases. Further, the work of various investigators on the influence of a trace of moisture on reactions between gases has demonstrated the effect which an undetectable trace of one kind of matter may have on systems which, without it, are incapable of change, and so, by analogy, has strengthened the position of the extreme ionist. The exceedingly interesting observations of Kahlenberg and his pupils (*Zeit. physikal. Chem.*, 1903, 46, 68) that hydrogen chloride and trichloroacetic acid react readily with some metals in certain non-ionising media have therefore been met, as it were, in anticipation, by the advocates of this theory, which assumes the presence of ions because a reaction takes place. However, to take refuge behind a mathematical abstraction which, from the nature of the case, is incapable of experimental demonstration, is a position that is decidedly unsatisfactory when another method of representation of the same phenomena suggests itself, at least until that other method has been shown experimentally to be untenable. A second and even more

vulnerable point of weakness in the theory is the tacit assumption of the absence of any extensive ionisation when no reaction is observable. Even with regard to the first, the argument would have a certain amount of force that in one of two otherwise parallel instances, neither of which exhibits ionisation, a reaction is found to take place with great readiness, whilst in the other it does not do so at all. An instance of this nature came under my observation in the behaviour of ethereal solutions of hydrogen chloride and of trichloroacetic acid towards zinc. The first evolves hydrogen vigorously even when no moisture is present, the latter not at all. The amount of ionisation is so small as to be immeasurable in both solutions, and the cases are so far parallel that in aqueous solution both acids are ionised to a very great extent. Is it legitimate, therefore, to assume ionisation in the first ethereal solution only? The second line of attack is of course open to the objection that the absence of reaction is due to the absence of the necessary kind of ions. But if instances can be brought forward which are so similar that the nature of the ions may in all be assumed to be the same, and if reaction takes place in some cases and not in others, it would seem advisable to look round for another method of representing the mechanism of the reactions in question. Such a method is found in the conception of potential valency as the determining factor in many chemical reactions, and, although very frequently brought forward, it has never received what seems to me due consideration, possibly because it has not been supported by any great weight of experimental evidence. In this and the following communications I hope to bring forward some observations which point to the necessity of such an assumption in special cases, as well as to discuss the closely-allied question of ionisation and chemical combination from the standpoint of cause and effect.

The possibility of a close relationship between these two series of phenomena, the combination of a solvent with the dissolved substance and the electrical conductivity of the resulting solution, was advanced even in the early days of the electrolytic dissociation theory by Ostwald (*Lehrbuch*, II, 1, 801). He states clearly, without laying special stress on the statement, that ionisation may be accompanied by a process of hydration, and, although this suggestion was at first neglected, a very intimate connection between the two series of phenomena has recently begun to be insisted on, notably by Bruhl, who sees in chemical combination not the concomitant or even the more or less accidental precursor of ionic dissociation, but the necessary condition for the existence of the latter.

Meanwhile two other properties of solvents were being considered in the same causal relationship, namely, the association of the solvent and its dielectric power. Dutoit and Friderich (*Bull. Soc. chim.*,

1898, [iii], 19, 321) concluded from their investigation on solutions in ketones and nitriles, as well as from the results observed by others in various other solvents, that a non-associated liquid has no ionising power. From the extensive series of researches which have been carried out in recent years by various investigators, among others by Walden, Kahlenberg, Carrarra, and Euler, on solutions other than aqueous, a summary of which is given by Walden (*Zeit. physikal. Chem.*, 1903, 43, 388), it appears that this view regarding the connection between its degree of association and the ionising power of a liquid is not generally applicable. Lincoln (*J. Physical Chem.*, 1899, 3, 486), in discussing the possibility of such a connection between the two phenomena, states that some solvents, which show at most only very slight association, yield solutions that conduct quite well, whereas others, the molecules of which are to some extent polymerised, do not form conducting solutions. The question of the non-association of certain liquids is, however, one regarding which different views may still be held. Ramsay, assuming the simplest molecular formula for some, was able to compute the relative complexity of others, but it may well be doubted whether any ordinary liquid consists for the most part of simple molecules, although with our present hard and fast conceptions of the strictly limited valency of certain elements it seems necessary to assume that the hydrocarbons of the marsh gas series at least must be so constituted. Some experiments on heats of solution, described elsewhere by the author (*Proc. Roy. Soc. Canada*, 1902, 7, [iii], 105), may be considered as throwing doubt at least on this assumption. Certainly, however, the accepted degree of association of a liquid seems to have no very intimate connection with the question as to whether it can or cannot yield conducting solutions. It is otherwise with respect to the dielectric power of a liquid, for, although there does not seem to be direct proportionality between the magnitude of the latter and the extent to which the liquid can ionise a substance dissolved in it, still, in general, liquids with high dielectric constants have been found thus far to yield solutions of the highest conductivity.

Although the accepted molecular complexity of a liquid is not a criterion of its ability to yield conducting solutions, there is a chemical property which may well be considered as essential to the exhibition of this phenomenon, namely, the presence of atoms in its molecule which show a marked tendency to enter into certain combinations where they exhibit a higher valency. As is well known, association is not dependent on the presence of such atoms. The range of substances which may be expected to be ionising media is therefore greatly extended. The possibility of chemical combination being a precursor of ionic dissociation seems to have been first experimentally con-

sidered by Konowaloff in an investigation on "Properties of the solutions which amines form with acids" (*Wied. Annalen*, 1893, 49, 733). In these cases the power of conducting the current is shown to be closely connected with the reactions which take place between acid and base.

Two causes, however, may have operated against the application of this idea of combination as the cause of ionisation, derived from the special case considered by Konowaloff, to the more common one of aqueous solution. Firstly, the molecular conductivity of electrolytes in the latter almost invariably increases with dilution, whilst that of the amines decreases in the same circumstances. This objection, however, lost its weight, although no definite conclusion was drawn regarding the causes operating to produce ionic dissociation, when it was shown by Kahlenberg and Lincoln (*J. Physical Chem.*, 1899, 3, 12) that in some instances which they treat as cases of simple solution, but where chemical combination undoubtedly occurs between the solvent and the solute, the molecular conductivity increases with dilution, whilst in others it diminishes. The second and main cause which prevented any analogy being drawn between solutions of amines in acids and of substances in aqueous solution was the lack of appreciation of the closeness of the resemblance between oxygen and its companions in the seventh group in the periodic table, although this had been very decidedly pointed out by van't Hoff (*Ansichten über die Organische Chemie*, 1877). So long as water was regarded as a saturated compound, in so far as ordinary chemical combining power is concerned, hydration could scarcely be considered, and was certainly not universally considered, to be a distinctly chemical phenomenon, and one likely to play an important rôle in the production of solutions possessed of the power of conducting electricity. In fact, although the higher valency of the oxygen atom had been repeatedly suggested as a simple means for associating a large number of otherwise more or less disconnected facts, Collie and Tickle (*Trans.*, 1899, 75, 716), when proposing the oxonium theory to account for the existence of the compounds of dimethylpyrone with acids, expressed the opinion that the tendency for oxygen to form definite compounds in which its higher valency is evident can at best be feeble, and that isolation of the compound can only be expected in favoured cases. A summary of the opinions regarding, and of the investigations on, this subject has recently been given by Walden (*Ber.*, 1901, 34, 4185, and 1902, 35, 1764), as well as by Schmidt (*Ueber die basischen Eigenschaften des Sauerstoffs und Kohlenstoffs*, 1904). The very great import of the conception, in its bearing on the mechanism of chemical reaction, was pointed out by Collie and Tickle, and the subsequent work of Baeyer and

others shows that amongst organic compounds the isolation of the desired derivatives may be an easier problem than was at first anticipated.

The conception regarding the mechanism of chemical reaction, according to which combination, in virtue of potential valency, precedes any manifestation of chemical change, is at least equally with that of ionic dissociation, as the necessary forerunner of reaction, in harmony with thermodynamical principles. It is not therefore necessary to attribute reaction between the most diverse kinds of substances entirely or mainly to a previous ionisation of these substances, especially when the existence of intermediate compounds, which may or may not be ionised, is so easily shown in many instances not only by actual isolation, but also by the irregular change of some physical property of their solutions. The actual isolation of an intermediate compound in special circumstances may, however, be rejected as proof of its actual participation in a given reaction under ordinary conditions, hence the frequent resort to dynamical studies as a means of determining the mechanism of certain reactions. An interesting class of reactions for study along both of these lines is that involving the interaction of the halogen hydrides and substances of the type  $R(OR_1)_n$ , where neither R nor  $R_1$  contains atoms to which change of valency is usually assigned, and where therefore the formation of an intermediate compound could only be attributed to the higher valency of oxygen, as in Friedel's compound of hydrogen chloride and dimethyl ether (*Bull. Soc. chim.*, 1875, 24, 241), and in the compounds of the ethers with the other halogen hydrides (*Ber.*, 1875, 8, 1352, and *Amer. Chem. J.*, 1898, 21, 64). The ethereal salts of such inorganic acids as phosphorous and boric acids were selected, and attempts were made to isolate compounds at very low temperatures, where their stability would probably be increased, as well as to measure the velocity of such reactions as  $PCl_3 + C_2H_5 \cdot OH = PCl_2 \cdot O \cdot C_2H_5 + HCl$ , also at low temperature, and in some indifferent solvent which might be assumed to have little attraction for either of the products of dissociation of the complex  $PCl_2(OHCl \cdot C_2H_5)$ . This investigation had proceeded some way and indications of the existence of compounds of this nature obtained, when it was observed by my assistants, Mr. McIntosh and Dr. Archibald, that a few substances of this type form good conductors when dissolved in the liquefied halogen hydrides, which have been lately shown by Steele and McIntosh (*Proc. Chem. Soc.*, 1903, 19, 223) to be ionising media for some ordinary electrolytes. Since the conductivity could only be ascribed to ionisation following on combination between solvent and solute, the method suggested itself as a very simple one for determining whether, in analogous cases at least, combination had taken place or not. The results of this investigation form the subject of another communication.

Even dynamical studies, however, do not yield a conclusive answer as to the nature of a reaction, but only elucidate that stage of it, the velocity of which is measured. The results may indicate that the chemical change proceeds by way of ionisation or by the formation of an intermediate complex, but, nevertheless, in neither case is the other excluded as an operative cause during a previous or a subsequent stage. For example, in the Friedel-Crafts reaction, lately studied in this laboratory, it has been shown by Steele (*Trans.*, 1903, 83, 1470) that, when benzyl chloride acts on an excess of toluene in the presence of aluminium chloride, the reaction is unimolecular, indicating the formation of a compound between the reagents. The method, however, gives no information as to whether this complex in its subsequent action reacts in the ionised condition or not, nor does it tell us whether the compound is formed by an ionic reaction from its constituents or by their direct union in virtue of potential valency. And, conversely, had the reaction been found to be bimolecular, it would not have excluded the possibility of the formation of an intermediate compound in some stage of the process. The considerations put forward in the foregoing pages gave rise to the following investigation.

#### EXPERIMENTAL.

It has been shown by Kahlenberg and Lincoln (*J. Physical Chem.*, 1899, 3, 19) that solutions of ferric chloride in *o*-nitrotoluene are fairly good conductors of an electric current, whilst solutions of the same salt in anisole conduct very poorly. This is in accord with the general behaviour of nitrohydrocarbons and of ethers. Gattermann has already indicated that both of these classes of substances combine with aluminium chloride, and a more detailed description of the compounds will be given in another communication. Measurements of the electrical conductivity of aluminium chloride in *o*-nitrotoluene and in anisole gave the following results at 18°,  $V$ , the volume, being expressed in litres, and  $\mu$ , the molecular conductivity, in reciprocal ohms.

In <i>o</i> -nitrotoluene.		In anisole.	
$V = 1.15$	$\mu = 0.6$	$V = 0.31$	$\mu = 0.026$
2.30	0.8	0.62	0.026
4.60	1.1	0.78	0.023
9.20	1.5	0.99	0.019
18.40	2.2	1.25	0.018
36.80	3.7	1.55	0.012
73.60	4.3	1.97	0.010
147.20	1.9		

In preparing these solutions, a quantity of aluminium chloride was distilled into the tube forming the conductivity cell, which was then

instantly corked up and weighed. The salt was dissolved in each case in 4 c.c. of the solvent, and from this solution the others were made by dilution in the ordinary way. No account has therefore been taken of the volume of the aluminium chloride. The molecular conductivity of the solution in *o*-nitrotoluene increases regularly with dilution, and, although the most dilute solution shows a large decrease, calculation indicates that, if, as is most probable, moisture would destroy the conducting power, a very small amount would be sufficient to produce the observed effect. With anisole, on the contrary, the molecular conductivity diminishes continuously with increasing volume, and this phenomenon will be discussed later. When these solutions are now compared with regard to their powers of reaction, it is seen that, as far at least as the Friedel-Crafts reaction is concerned, there is no connection between ionisation and reactivity, for, whilst *o*-nitrotoluene along with other nitrohydrocarbons is distinguished by its indifference in this respect, anisole is found to be extremely reactive (*Ber.*, 1890, 23, 1199), and yet its conductivity is found to be less than the 1/100th part of that of the *o*-nitrotoluene solution. The conclusion seems obvious that in this case reaction is conditioned by some factor other than ionisation. Evidently also, since both substances combine with aluminium chloride, what ionisation there is is consequent on chemical reaction; no antecedent ionisation can be detected either in *o*-nitrotoluene, anisole, or aluminium chloride.

A further observation of considerable interest was made when the solution of aluminium chloride in anisole was treated with benzoyl chloride, that is, was made to undergo the Friedel-Crafts reaction. The solution contained 1.286 grams of the chloride in 6 c.c., and when examined in the cell employed in the preceding experiment its resistance was found to be more than 50 times greater than that of 1/50 *N* potassium chloride. When, however, 1 c.c. of benzoyl chloride was added and the ensuing reaction had ceased, its resistance at the same temperature was found to be somewhat less than that of the same potassium chloride solution. The amount of benzoyl chloride added is slightly less than equivalent to the aluminium chloride, but, assuming it to be equivalent, the molecular conductivity of the resulting compound of the ketone with aluminium chloride has been calculated:  $V = 0.727$ ,  $\mu = 2.0$ ;  $V = 1.142$ ,  $\mu = 2.3$ .

The first conclusion from this experiment is that there has again been chemical action with a consequent large increase of electrical conductivity, and therefore also presumably of ionisation; the second, that, with an appropriate solvent, anisole yields solutions which conduct quite as well as the solutions in *o*-nitrotoluene, although thus far it has been looked on as a practically non-ionising medium. Further, although it was examined only at two concentrations, the

conductivity seems to increase with dilution in the normal manner. Another remark, which has reference to the cause of the chemical reaction, may be added, namely, that, although the ionic concentration is now considerable, further addition of benzoyl chloride causes neither further change of conductivity to any marked extent, nor does it produce further chemical change. A similar result to the above was obtained by substituting acetyl for benzoyl chloride. Unfortunately, the occurrence of well-known reactions prevents the employment of these acyl chlorides as solvents for aluminium chloride, but thionyl chloride was substituted. No quantitative experiment was performed, but it was observed that, whilst some aluminium chloride in this solvent had a resistance in the same cell of 35,000 ohms, the addition of a little naphthalene caused it to fall to about 2500 ohms. In this case also, ionisation seems to be greatly increased by reaction, although not to the same extent.

*Metathetic Reactions between the Alkyl Halides.*—In attempting to prepare some simple compounds of the alkyl halides with aluminium chloride, it was observed that, whilst this salt is apparently only slightly soluble in ethyl iodide or chloroform separately, it is rapidly dissolved when added to a mixture of these two substances. The liquid at once becomes dark red, and in a short time an abundant crystalline deposit of iodoform separates. Similar results were obtained when methyl iodide was substituted for ethyl iodide and carbon tetrachloride for chloroform, carbon tetraiodide being the solid product in the latter case. The aluminium chloride evidently combines very readily with a mixture of two of these substances forming a very dark red compound, which, in the case of ethyl iodide, is quite soluble, but in the case of methyl iodide could be seen as a dark, supernatant layer. A relatively small quantity of aluminium chloride was sufficient to convert a large amount of methyl iodide into carbon tetraiodide or iodoform. Although instances of double decomposition between aluminium halides and a single alkyl halide are on record, and in the case of carbon tetraiodide this reaction is the one employed for its production from carbon tetrachloride and aluminium iodide (*Annalen*, 1874, 172, 173), an apparently catalytic reaction proceeding with such facility between two substances which, under ordinary conditions are so indifferent to each other as ethyl iodide and carbon tetrachloride, seemed to warrant a little further investigation. The first point of interest is the manifest display of the higher valency of the halogen atoms in the formation of the soluble or liquid double compounds. No results have been obtained thus far in the few attempts made at a closer characterisation of these compounds. The matter is one of considerable difficulty, since one of the products of their dissociation is gaseous and very likely readily split off, and

another is a somewhat soluble solid. Further, there are grounds for believing that the aluminium chloride is partially converted into iodide during the reaction. This introduces a further complication. Meantime an outline of the course of the reaction in two cases will be given.

To a mixture of 5 grams of chloroform and 20 grams of ethyl iodide was added 0.385 gram of aluminium chloride. The substances were therefore present in the molecular ratio 1:3:0.07. The reaction was performed in a flask closed with a stopper which carried a fine capillary tube to allow the ethyl chloride produced to escape and to prevent the entrance of air and moisture. After several hours, practically all trace of liquid had disappeared, leaving only iodoform in the flask. The yield was almost quantitative. To a mixture of 12 grams of carbon tetrachloride and 48 grams of ethyl iodide, 1 gram aluminium chloride was added. The substances are in the molecular ratio 1:4:0.1. The salt was dissolved rapidly and a brisk effervescence set in, due to the escape of ethyl chloride. In less than half an hour the comparatively small quantity of residual liquid was decanted from the heavy, red, crystalline deposit which had formed very rapidly. The latter was quickly washed with alcohol and water and was identified as pure carbon tetraiodide. The reaction with methyl iodide is much slower than with ethyl iodide, doubtless owing to the slight solubility of the intermediate compound, and consequently the carbon tetraiodide was obtained in much larger crystals. Experiments were also made in order to determine if the same reaction could be induced by phosphorus trichloride, silicon tetrachloride, and boron trichloride, but the results were negative. Ethyl bromide was also substituted for ethyl iodide in the expectation that carbon tetrabromide would be obtained with the same facility. The aluminium chloride dissolved forming a red liquid, but when left for two days in a flask arranged as before there was no appearance of crystals. After six weeks, a few crystals in the form of transparent plates had separated, but very little liquid had evaporated. The reaction in this case is evidently excessively slow.

*Electrical Conductivity in the Alkyl Halides.*—Solutions of various substances, which in other media conduct well, have been examined in the alkyl halides by Dutoit and Aston (*Compt. rend.*, 1897, 125, 243), Kahlenberg and Lincoln (*J. Physical Chem.*, 1899, 3, 19), and Patten (*J. Physical Chem.*, 1903, 7, 161), but have been found to show no electrical conductivity. Kahlenberg and Lincoln employed ferric chloride as the solute, and therefore there was but little expectation that, since it gave negative results, a positive one would be obtained with aluminium chloride, the more so as these liquids, in view of their very

low dielectric power would not be expected from the Nernst-Thomson generalisation to yield conducting solutions. Their very pronounced chemical activity, however, in presence of that salt made it essential to test the point experimentally. With methyl, ethyl, and *n*-propyl iodides, as well as ethyl bromide and chloroform, considerable conductivity could readily be detected, but only in the case of ethyl bromide was the resistance of the solution, saturated with aluminium chloride, found to be less than 2000 ohms in the same cell as was used previously. Accordingly this alone was examined quantitatively with the following result:  $V = 1.6$ ,  $\mu = 0.7$ ;  $V = 3.2$ ,  $\mu = 0.4$ .

The conductivity is low and decreases with dilution. The lower conductivity in ethyl iodide was most probably due to slight solubility, since, when a little chloroform or carbon tetrachloride was added so as to bring the excess of salt into solution, the resistance diminished greatly. Quantitative determinations by this method were excluded by the deposition of solid on the electrodes. The results seem to point to the conclusion that the catalytic reaction just described is an ionic reaction, and this in media where previously the existence of ions had not been demonstrated. One consideration, however, throws doubt on this conclusion. In a mixture of ethyl bromide and carbon tetrachloride, the aluminium chloride seems to conduct just as well as if ethyl iodide was substituted for the bromide, and yet, as was shown, the corresponding reaction with the bromide is very much slower. Further, the observed ionisation is itself the result of chemical combination when a mixture of alkyl halides is employed as solvent. The facts agree much better with the hypothesis of an intermediate compound which undergoes rearrangement to a more stable system, the method of rearrangement depending on a molecular, and not on an accidental, ionic dissociation of the complex.

*Ionisation in the Friedel-Crafts Reaction.*—Since the solutions of aluminium chloride in the alkyl halides had been found to be conducting liquids, it seemed quite likely that further chemical action might, as in the case of anisole, produce liquids of higher conducting power. Accordingly, to a solution of aluminium chloride in ethyl bromide, which showed in the same cell as before a resistance of 2770 ohms, a little benzene was added. A reaction immediately occurred with an evolution of hydrogen bromide, but after this had ceased the resistance of the solution was found to have decreased to 220 ohms. Similarly, to a solution of aluminium chloride in ethyl bromide, which showed a resistance of 1630 ohms, a little naphthalene was added, when the resistance fell to 92 ohms.

These results are conclusive enough as regards the dependence of

ionisation on chemical reaction, but they do not indicate in any way the dependence of chemical reaction on ionisation.

Some points of equal interest were observed in what is so far a somewhat roughly quantitative study of these cases. A solution was prepared containing 1 gram-molecule of benzene to 1 gram-molecule of aluminium chloride, the solvent being ethyl bromide. A slight evolution of an acid gas occurred immediately when the solvent was added, and a straw-coloured liquid remained when the whole of the salt had disappeared. This was diluted in the ordinary way as the measurements of conductivity were made. A corresponding series was made with naphthalene.

Benzene.		Naphthalene.	
$V=0.907$	$\mu=4.2$	$V=1$	$\mu=3.9$
1.814	1.5	2	2.3
3.628	5.7	3	4.9
7.256	4.3	4	5.4
		8	3.5

The volume is assumed to be the sum of that of the ethyl bromide and of the benzene or naphthalene, and the molecular conductivity  $\mu$  is calculated on the aluminium chloride present. In both cases, its value is observed to pass through a minimum with increasing volume—in fact, even the observed conductivity does so—and then through a maximum, and there is an indication that the position of those points in the case of benzene may be identical with their position in the case of naphthalene. With the latter, the evidences of chemical change are very marked. Thus, at  $V=1$ , the colour was very deep red, at  $V=2$ , still deep red, at  $V=3$ , medium red, at  $V=4$ , quite pale, and at  $V=8$  almost colourless. As will appear in the sequel, points of sharp colour change correspond with these positions of maxima and minima in the curves of molecular conductivity. In the following experiments, aluminium chloride was added in small quantities to a solution of benzene or naphthalene in ethyl bromide, and repeated measurements of the conducting power of the solution were made in the same cell as before, while the salt slowly dissolved. In this way, the position of the points of maximum and minimum conductivity could be gauged with a fair degree of accuracy even in the first experiments.

## I. Benzene; 0.4311 gram in 4 c.c. of ethyl bromide.

AlCl <sub>3</sub> .	Resistance in ohms.		V.	μ.
0.0532 gram	3300	colourless		
	3000	„	11.3	1.38
0.1788 „	400	„		
	390	„	3.4	3.2
0.2500 „	355	„		
	367	„ slight fume	2.4	2.4
0.3214 „	750	„		
	1800	„		
	3400	„ { almost all dissolved }	?	[0.13]
	2000	pale yellow		
	1900	„	1.87	0.35
0.4170 „	207	deeper yellow		
	197	„	1.44	2.7
0.5185 „	101	„	1.16	4.3
0.8570 „	43	effervescence	0.7	6.0
1.1630 „	35	„	0.52	5.5

The appearances accompanying these remarkable changes in conductivity are much less pronounced in the case of benzene than in that of naphthalene, but are still quite distinctly evident. Thus, neither colour nor acid fume is observed until the first maximum is reached, when a slight acid fume becomes perceptible. This continues and the solution remains quite colourless until the minimum is just passed, when a yellow colour appears quite suddenly. This continues to deepen, still without any effervescence of acid gas, until more than an equivalent weight (0.7378 gram) of aluminium chloride, calculated on the benzene present, has been added. Apparently in this neighbourhood a maximum of conductivity is again reached. The position of the minimum coincides very nearly with a volume of 1.87 litres, and, taking the highest resistance recorded when only a trace of salt was left undissolved, the molecular conductivity is found, with only a slight error, to be 0.13, or about one-thirtieth of the previous maximum. Whether these sharp changes of conductivity point to the formation of definite compounds between the aluminium chloride and the benzene, or the ethyl bromide or both, will be discussed after the observations with naphthalene have been described.

## II. Naphthalene; 0.6459 gram in 4 c.c. of ethyl bromide.

AlCl <sub>3</sub> .	Resistance in ohms.	V.	μ.
0.0302 gram	14000 colourless	20	0.53
0.0577 „	4100 „	10.4	0.95
0.1209 „	1240 „	5.0	1.5
0.3134 „	1950 orange		
	2100 „ slight fume		
	2210 „	1.92	0.32
0.3692 „	408 deep red		
	385 „	1.63	1.57
0.4532 „	140 „	1.33	3.5
0.5634 „	85 „	1.06	4.6

In this experiment, there was never any effervescence due to the escape of hydrogen bromide. This point would probably have been reached by adding an equivalent weight of aluminium chloride, namely, 0.6735 gram. A second series of observations was made in order to locate the maximum and minimum points more closely. The continual fall from the first values for  $\mu$  shows, however, that the maximum had been already reached in the first observation.

AlCl <sub>3</sub> .	Resistance in ohms.	V.	μ.
0.2300 gram	527 colourless	2.61	1.85
0.2408 „	531 pale pink	2.5	1.75
0.2530 „	558 „	2.37	1.58
0.2823 „	700 „	2.13	1.13
0.3078 „	980 „		
	1480 „	1.95	0.49
0.3187 „	2155 „		
	3390 „	1.88	0.21
0.3247 „	5670 red		
	5900 „		
	5757 „	1.85	0.12
0.3272 „	5210 very deep red	1.84	0.13
0.3350 „	2500 „		
	1970 „	1.79	0.34

In this series of observations, in which the aluminium chloride was added in very small portions, the colour changes are seen to be exceedingly sharp. For example, 1 centigram induces a pale pink tinge in the colourless solution, whilst less than 8 milligrams trans-

forms the pale pink into a very deep red. When the position of the minimum for naphthalene is compared with that for benzene it is found that they lie very close together—about  $V=1.85$ —and when the amount of aluminium chloride added up to that point is compared with the quantity of naphthalene present it is found that they are very nearly in the ratio of one molecule of the former to two of the latter. With benzene, however, the agreement is not so close if the position of the minimum value is taken as identical with that for naphthalene. Again, in the second series of observations with the latter substance, the first reading is probably very close to the maximum, since colour develops with the addition of less than 1 centigram of aluminium chloride. If so, this maximum corresponds almost exactly with a molecular ratio of three of naphthalene to one of aluminium chloride. The breaks in the curves would therefore seem to indicate the formation of compounds  $3X, AlCl_3$ ,  $2X, AlCl_3$ , and  $X, AlCl_3$ , where  $X$  stands for a molecule of hydrocarbon. As a test of the cogency of this conclusion, the proportion of naphthalene present was also varied with the following result.

### III. Naphthalene ; 1.2918 grams in 4 c.c. of ethyl bromide.

$AlCl_3$ .	Resistance in ohms.	$V$ .	$\mu$ .
0.0625 gram	10400 colourless	11.32	0.4
0.1584 „	1800 „	4.46	0.9
0.1910 „	1200 „	3.70	1.15
0.2690 „	800 „		
	800 faint pink	2.63	1.23
0.2816 „	860 „	2.51	1.08
0.3520 „	4230 red		
	4000 „	2.01	0.18
0.4470 „	315 very deep red	1.58	1.87
0.5120 „	177 „	1.38	2.90
0.8695 „	70 „	0.81	4.32

There was still no effervescence due to escape of hydrogen bromide.

## IV. Naphthalene; 0.6459 gram in 8 c.c. of ethyl bromide.

$\text{AlCl}_3$ .		Resistance in ohms.	$V$ .	$\mu$ .
0.0880	gram	6670 colourless	12.9	0.96
0.1540	"	2580 "	7.37	1.06
0.1937	"	1874 "	5.86	1.16
0.2720	"	980 "	4.17	1.58
0.3630	"	575 "	3.13	2.02
0.5994	"	445 faint pink		
		724 "	1.80	0.93
0.6836	"	1820 very deep red		
		1000 "	1.66	0.65
0.7704	"	277 no effervescence	1.47	1.98

It is evident that in every instance the minimum is situated at very nearly, if not exactly, the same point, namely, at 0.32 gram of aluminium chloride to 4 c.c. of ethyl bromide, and this independently of the nature of the hydrocarbon and also of its amount. There are not sufficient data to warrant the same conclusion with regard to the point of maximum conductivity, which seems to correspond approximately with 0.23 gram of aluminium chloride to 4 c.c. of ethyl bromide, but if there is a variation it is within comparatively narrow limits. This observation does not bear out the conclusion that the maxima and minima indicate the existence of compounds between the hydrocarbon and the aluminium chloride. It points rather to the presence of some other substance or substances in the ethyl bromide which react first with the aluminium chloride, producing colourless or only slightly coloured solutions. As ordinary ether is an impurity of this nature which might be present, although the ethyl bromide had been very carefully washed with water, the liquid was shaken repeatedly with concentrated sulphuric acid, then with dilute caustic potash, and finally with water. After this treatment it no longer showed the same phenomena when employed as a solvent for naphthalene and aluminium chloride. On the contrary, the first small addition of the latter produced a deep red coloration, whilst the conducting power of the solution was found to be even greater than before, and to increase steadily with increasing concentration of salt.

## V. Naphthalene; 0.8074 gram in 5 c.c. of ethyl bromide.

$\text{AlCl}_3$ .		Resistance in ohms.	$V$ .	$\mu$ .
0.0220	gram	2730 deep red	30.34	4.44
0.0420	"	1128 "	15.90	5.64
0.0870	"	390 "	7.67	7.84
0.1795	"	161 "	3.72	9.23
0.3335	"	80 "	2.00	10.20
0.3660	"	70 "	1.82	10.48
0.4050	"	60 "	1.65	10.86
0.4880	"	50 "	1.37	10.88
0.5445	"	47 "	1.226	10.40

A very strong indication that ether is the disturbing agent in the previous experiments was found by adding a known quantity of ether to the purified ethyl bromide both with and without naphthalene. In both instances there was a maximum and a minimum of conductivity as the aluminium chloride was gradually added, and, when the concentration of the ether was the same in both, the minimum was reached when identically the same amount of aluminium chloride had been added to each. It was also found that when the amount of ether present was varied, the amount of aluminium chloride required to produce the minimum varied proportionately. Further, the position of the minimum corresponds accurately with the ratio of 1 mol.  $\text{AlCl}_3$  to 1 mol.  $\text{C}_4\text{H}_{10}\text{O}$ . The aluminium chloride therefore combines with the ether entirely before it attacks the ethyl bromide. The position of the maximum is not so well defined; it is conditioned by the equilibrium between the very poor conductor  $\text{AlCl}_3, \text{C}_4\text{H}_{10}\text{O}$  and the fairly good conductor  $\text{AlCl}_3, x\text{C}_4\text{H}_{10}\text{O}$ . The observations in Table II would seem to indicate that  $x$  may have the value 1.5. It is very remarkable that the resistance of the solution containing  $\text{AlCl}_3, \text{C}_4\text{H}_{10}\text{O}$  is more than ten times greater than that containing  $\text{AlCl}_3, x\text{C}_4\text{H}_{10}\text{O}$ .

By the addition of aluminium chloride, representatives of two classes of substances, namely, the alkyl halides and the aromatic hydrocarbons, which thus far have been regarded as media incapable of sharing directly in the production of ions, have been shown to become good conductors. The conductivity has been traced to the formation of compounds in virtue of the potential valency of certain atoms which they contain. The formation of these compounds and their comparative stability in the Friedel-Crafts reaction is evidenced by the fact that very little acid is evolved until the concentration of the aluminium chloride passes a certain value. In some instances,

therefore, the proof seems conclusive that chemical reaction is the cause and ionisation the effect of subjecting the substances selected to those reactions to which experience has shown them to be peculiarly liable. This consideration suggested the possibility that these or similar compounds might conduct even when dissolved in the hydrocarbons. No trace of conductivity could, however, be detected in benzene to which aluminium chloride and ethyl bromide had been added. The lower layer which separates when sufficient amounts of the two latter substances are employed is quite a good conductor, but this is not in benzene solution. In a qualitative experiment it was found that bromobenzene can yield solutions possessed of some conductivity.

In various instances it has been shown, as is the case with solutions of aluminium chloride in anisole, that the molecular conductivity diminishes instead of increasing with dilution. Sackur (*Ber.*, 1902, 35, 1248), who examined a few examples of this kind, attributes the latter only to combination with the solvent. This seems to be an arbitrary distinction, however, as there is no reason why progressive combination should not yield a compound more ionised than the original instead of, as he assumes, yielding one less ionised. The foregoing examples of maxima and minima seem to illustrate this.

This investigation will be continued and extended.

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## CXII.—*Ionisation and Chemical Combination in the Liquefied Halogen Hydrides and Hydrogen Sulphide.*

By JAMES WALLACE WALKER, DOUGLAS McINTOSH, and EBENEZER ARCHIBALD.

As was indicated in the preceding communication by one of us, recent investigation points to the conclusion that ionisation is dependent on chemical combination between solvent and dissolved substance, although it is by no means a necessary consequence of the latter. The recent investigation by Steele and McIntosh (*Proc.*, 1903, 19, 223) on the ionising power of the liquefied halogen hydrides for some ordinary electrolytes led to the examination in these media of a variety of substances which are not electrolytes in aqueous or alcoholic solution. It rapidly became apparent that results were being obtained entirely in harmony with the considerations set forth in the preceding com

munication, namely, that ionisation is subsequent to chemical combination with the solvent, and that, at least in some instances, the latter phenomenon is to be ascribed to potential valence. The method of conductivity measurement suggested itself therefore as a possible one for ascertaining whether, in analogous cases at least, combination had taken place or not. As a very large number of the organic substances, which have been found to yield conducting solutions in these media, contain oxygen, instances were selected where combination could only occur in virtue of the higher valency of the oxygen atom. Examples of this class are not numerous, being restricted to the type  $R(OR_1)_n$ , which includes alcohols, ethers, acetals, and the ethereal salts of some mineral acids. The tendency of aldehydes, ketones, acids, and their chlorides, amides, ethereal salts, &c., to form additive compounds can always be represented, of course, as being due to the presence of a double linking in the molecule. On extending the range of the investigation to include substances, which undoubtedly do combine with these solvents, it was found that many of the resulting solutions either did not conduct at all or only to a very slight degree. It was evident therefore that, although this method might give indication of combination when conductivity was observed, absence of the latter property does not exclude the possibility of combination in the act of solution.

A series of observations were also made on solutions of the same organic substances in liquefied hydrogen sulphide. This liquid was found to be possessed of a remarkable solvent power for nearly all the substances examined in it, but only in a very few instances, and in those cases in which combination undoubtedly occurs, were the solutions possessed of much conductivity.

#### EXPERIMENTAL.

The method employed was the ordinary one with Wheatstone's bridge and telephone; about 4 c.c. of the solvent were placed in a small conductivity cell, and, after establishing the purity of the solvent by a measurement of its resistance, about 4 drops of the liquid or a few powdered crystals of the solid solute were added, and after solution and mixing a reading was again made. The temperature employed varied with the solvent, namely,  $-100^\circ$  for hydrogen chloride,  $-80^\circ$  for hydrogen bromide and hydrogen sulphide, and  $-50^\circ$  for hydrogen iodide. It was maintained approximately constant throughout these qualitative measurements by a bath of solid carbon dioxide and ether boiling either under the ordinary or reduced pressure. In the following table, there is placed under the name of the solvent a symbol to designate the extent to which the solution of the substance named in

the first column conducts. Thus (+ + +) signifies a very good conductor, (+ +) fairly good, (+) good, (- +) poor, (- - +) very poor, and (-) a non-conductor.\* The letter C placed after the symbol denotes that there was very distinct evidence of the formation of a compound, either by the separation of a solid substance or by the violent action which accompanies solution causing the evaporation of a considerable amount of the solvent. Only in a very few instances is the absence of conductivity to be attributed to insolubility, since the great majority of the substances were seen to be readily soluble in all four solvents. In the sixth column of the table there is also placed for the purpose of comparison a series of observations made by Kahlenberg and Lincoln (*J. Physical Chem.*, 1899, 3, 19) when using these organic liquids as solvents for ferric chloride.

	HCl.	HBr.	HI.	H <sub>2</sub> S.	FeCl <sub>3</sub> .
Toluene .....		-	-	-	-
Cumene .....		-			
Thiophen .....	++	++	-	-	
Pyrrole .....	+++ C.	++	++	-	
<i>n</i> -Butyl iodide .....		-	-	-	
<i>iso</i> Butyl iodide .....		-		-	
Ethylene dibromide .....		-		-	
Chloroform .....		-		-	-
Benzyl chloride .....		-		-	-
Benzylidene chloride ..		-		-	-
Bromobenzene .....		-		-	-
Formic acid .....	++	-		-	
Acetic acid .....	++	-		-	
Propionic acid .....	++	- +		-	
Chloroacetic acid .....	- +	-	-	-	
Bromoacetic acid .....	- - +	++	- +	-	
Trichloroacetic acid .....	-	-	-	-	
Cyanoacetic acid .....	- +	-		-	
Benzoic acid .....	+	- +			
Ethyl acetate .....					++
Amyl acetate .....	+++	++	++	-	
Methyl propionate .....		++		-	
Ethyl oxalate .....		++		- - +	++
Ethyl malonate .....		++			
Ethyl benzoate .....	++				+
Methyl mandelate .....	++				
Ethyl acetoacetate .....		++	++	-	++
Triethyl borate .....	++				
Ethoxyphosphorous chloride .....	++				

\* The substances of highest conducting power, designated by the symbol (+ + +), showed about the same conductivity as a *N*/50 aqueous solution of potassium chloride at 25°.

	HCl.	HBr.	HI.	H <sub>2</sub> S.	FeC <sub>3</sub> .
Acetyl chloride .. .. .	++	++	-	-	++
Acetyl bromide .. .. .	++	+	-		
Acetonitrile .. .. .	+++	+++	-+	+	
Benzonitrile .. .. .					++
Acetamide .. .. .	+++	+++	-+	-	
Urea .. .. .		++	+	-	
Acetanilide.....		++		-	
Methyl alcohol .. .. .	+++	+++	+++ C.	--+	++
Ethyl alcohol.....		+++ C.			++
Ethylene glycol.....				--+	++
Glycerol .. .. .		+		-	++
Mannitol.....		-		-	
Phenol.....	-	+ C.		-	+
<i>o</i> -Cresol .. .. .	-+	++	-+	-	
<i>m</i> -Cresol.....					+
<i>p</i> -Cresol .. .. .		++		-	
Quinol.....		-+		-	
Pyrogallol .. .. .		-		-	
Ether .. .. .	++ C.	++ C.	++ C.	-	-
Anisole .. .. .	++ C.	+	-	-	+
Anisaldehyde.....		++ C.	++ C.	--+	
Furfuraldehyde .. .. .		++	+ C.	-+	++
Enanthaldehyde .. .. .	++	++	-+	-	
Benzaldehyde.....		++ C.	++ C.	-	++
Para-acetaldehyde.....				-	++
Trithioformaldehyde.....			-+	-	
Acetone .. .. .	++ C.	++	++	-+	++
Methyl propyl ketone ...		++		--+	++
Acetophenone .. .. .		++		-	++
Phenyl ethyl ketone.....		++		-	
Benzophenone .. .. .		++	++ C.	-	
Benzil .. .. .		++	- C.	-	
Benzoin .. .. .	+++	++	-	-	
Amyl nitrite .. .. .		++	++	-	++
Nitrobenzene .. .. .		++	++	-	++
<i>o</i> -Nitrotoluene .. .. .	++	++		-	++
<i>p</i> -Nitrotoluene .. .. .		++		-	
<i>m</i> -Dinitrobenzene .. .. .		++		-	
<i>o</i> -Nitrophenol .. .. .	-+	-+	-+	-	
Picric acid .. .. .		-			
<i>m</i> -Nitraniline .. .. .	- C.	-		-	
<i>p</i> -Nitraniline .. .. .		-		-	
Aniline .. .. .		- C.	-+	-	+
Methylaniline .. .. .	++ C.	++		-	+
Dimethylaniline .. .. .	++	++	++ C.	-+	+
Diethylaniline .. .. .		++		-+	
Diphenylamine .. .. .		++		-	
<i>p</i> -Toluidine .. .. .		-	-	-	
$\alpha$ -Naphthylamine .. .. .		-	-	-	
$\beta$ -Naphthylamine .. .. .		-+	-	-	

	HCl.	HBr.	HI.	H <sub>2</sub> S.	FeCl <sub>3</sub> .
Phenylhydrazine .....		- + C.		-	-
Michler's ketone (tetramethyldiaminobenzo-phenone).....		- +	- +	-	
Pyridine .....		+ +	+ +	+ +	+
Piperidine .....		- +		+	
Quinoline .....		+ +		+	+
Nicotine .....		- +	+ + C.	+ +	
Strychnine.....		-		-	
Azoxybenzene .....		- +	-	-	
Azobenzene .....		- +	-	-	
Diisobutylamine .....				+	

Since the results with hydrogen sulphide are almost uniformly negative they may be disposed of briefly. Four substances which show considerable conducting power in this solvent are pyridine, piperidine, nicotine, and quinoline—all basic substances that certainly do combine with the solvent forming a sulphide, which might be expected to exhibit a certain degree of ionisation in a dissociating medium. The same remark applies possibly to the only other good conductor, acetonitrile, for the nitriles show a distinctly basic tendency. It is remarkable, however, that of all the other aromatic bases examined only dimethyl- and diethyl-anilines exhibit any conductivity and these only feebly. Four other substances show slight conducting power, and they also belong to classes which are capable of reacting with the solvent, namely, aldehydes and ketones. Of all the other types of organic compounds represented in the above list, possibly none shows any tendency to react with hydrogen sulphide, and only three substances show any conductivity, and that but very faintly. They are methyl alcohol, glycol, and ethyl malonate. All three might be represented as dissociating into a positive hydrogen ion and a complex negative one, but there is also the possibility that in virtue of the oxygen atom, which they all contain, the dissociated substance is an additive compound. From the results with hydrogen sulphide, we can only conclude that, since a few substances are good conductors in its solutions, the additive compounds with others, if formed, are only very slightly liable to electrolytic ionisation in this medium.

The behaviour of the halogen hydrides as solvents for the same substances is much more varied and interesting than that of hydrogen sulphide. With the exception of the hydrocarbons and their halogen derivatives, it may be stated roughly that all the substances examined containing the elements oxygen, nitrogen, and sulphur behave in one or other of these solvents as fairly good conductors, and even in the

class of hydrocarbon the allied substances thiophen and pyrrole are found to be good conductors. They doubtless combine with the solvent to form salts which then undergo ionisation. But even here a peculiar selective property is manifest, for whilst pyrrole is a good conductor in all three solvents, thiophen dissolved in hydrogen iodide does not conduct. Examples of the same phenomenon are seen in nearly every group of substances examined. A few of the more striking cases are arranged in the following table :

	HCl.	HBr.	HI.
<i>o</i> -Cresol .....	- +	+ +	- +
Formic acid.....	+ +	-	
Propionic acid.....	+ +	- +	
Bromoacetic acid .....	- - +	+ +	- +
Acetyl chloride .....	+ +	+ +	-
Acetamide .....	+ + +	+ + +	- +
Acetonitrile.....	+ + +	+ + +	- +
Anisole.....	+ +	+	-
Enanthaldehyde .....	+ +	+ +	- +
Benzoin .....	+ + +	+ +	-

In most instances, hydrogen chloride seems to yield solutions of highest, and hydrogen iodide solutions of lowest conductivity, but this is not general, for both *o*-cresol and bromoacetic acid conduct much better in hydrogen bromide than in hydrogen chloride, and nicotine better in hydrogen iodide than in hydrogen bromide. Further, there is a distinctly selective action between substances of the same type towards one solvent. This might to some extent be anticipated, but it exhibits itself in a somewhat peculiar manner. For example, the monohydric phenols and the nitrohydrocarbons both conduct well in hydrogen bromide; one might therefore expect the nitrophenols to be even better conductors, but such is not the case; *o*-nitrophenol conducts very little and picric acid not at all in that solvent.

The most interesting problem which suggests itself, however, with regard to these results is the nature of the substance which undergoes ionic dissociation. Walden has attributed most of the instances which came under his observation when using liquid sulphur dioxide as solvent to an ionisation of the original material, and not to that of a compound between the solvent and solute. This explanation might apply to some of the foregoing instances, but it would lead us beyond the extreme limits of analogy to apply it in all cases, and assign to such substances as thiophen, pyrrole, ethers, acid chlorides, ethereal salts, aldehydes, ketones, or nitrohydrocarbons a degree of ionisation comparable to that which is found in aqueous solutions of salts.

Further, the actual formation of compounds of most of these classes of substances either with the halogen hydrides or with metallic halides is well known and was often indicated during this investigation by a violent reaction on solution, or even by the separation of a solid compound. In some instances where the reaction was particularly violent, a considerable amount of the organic substance was added in the hope of isolating the compound formed. For example, the solid methyl mandelate was dissolved in large quantity by hydrogen chloride, but only a syrupy liquid was obtained, which could not be brought to crystallisation at a temperature above that of the freezing point of the solvent. In the case of ether and hydrogen iodide, however, a solid substance was easily isolated. The explanation of these phenomena most in harmony with all known facts is, therefore, that even the substances containing oxygen unite with the halogen hydrides to form salts, many of which dissociate in the excess of the solvent. Whether those which dissolve, but do not yield conducting solutions, also combine with the solvent is one of the many points in this inquiry which requires further investigation. For the present, it is sufficient to remember that the halogen compounds of some metals in aqueous solution are practically non-electrolytes, whilst those of others are among the best conductors in the same medium.

As was pointed out at the commencement of this communication, the constitution of such additive compounds can in most instances be ascribed to the presence of a double linking pre-existing in the molecule. But there are a few cases in which this representation of the structure of these substances is not applicable. Alcohols, phenols, ethers, and two ethereal salts, namely, ethyl borate and ethoxyphosphorous chloride, can only form additive compounds in virtue of a potential valency or valencies, and in all except the last-named substance the only probable atom to which this property can be attributed is the oxygen atom.

A comparison of the substances which conduct in the halogen hydrides with those which yield conducting solutions when ferric chloride is dissolved in them shows a very great degree of similarity. The only striking exceptions are the ethers, although even anisole manifests some conductivity when ferric chloride is dissolved in it, and has been shown in the previous communication to be capable under the necessary conditions of very considerable ionising power. Now the classes of compounds thus yielding conducting solutions are evidently such as will very likely be found to yield compounds with ferric chloride, since they do so with aluminium chloride. In this case also, conductivity is therefore to be attributed to ionisation following on combination. The same statement applies to many at least of the observations of Franklin and Kraus (*Amer. Chem. J.*, 1900,

23, 277) on the conductivity of solutions in liquid ammonia. As their observations on many organic substances are not given in detail, we have not cited them, but it appears that many of the substances which conduct are just such as are likely to react with the solvent, for example, aldehydes, ethereal salts, phenols, nitrophenols, and possibly dinitrobenzene. In this connection, it is of interest to record a few observations which we have made on that solvent. Methyl, ethyl, *n*-propyl, and *n*-butyl iodides, as well as ethyl bromide, show at first, when dissolved in liquid ammonia, only a slight conductivity, which, however, rapidly increases until the solutions conduct quite well. In the case of methyl iodide and ethyl bromide, the formation of an amine could be easily shown after evaporation of the solution. Carbon disulphide also dissolves in liquid ammonia to form a solution possessed of high conducting power. Most probably the solution contains in this case ammonium dithiocarbamate. Ether, on the other hand, shows no conductivity.

The conclusion we feel justified in drawing from these observations is that in at least a great number of cases, if not in all, combination with the solvent is the necessary precursor of ionisation, although such combination does not necessitate ionisation.

If the existence of these compounds between substances containing oxygen and the halogen hydrides is due in any way to their increased stability at low temperatures, comparison of the ammonium and oxonium theories suggests the possibility that at low temperatures such substances as alcohol or ether may add on alkyl iodides to form oxonium iodides. To test this, ethyl iodide was dissolved in ethyl alcohol at  $-100^{\circ}$ , but no conductivity was observed even after an hour. Ether was then added to the solution, but still it remained a non-conductor.

Quantitative measurements of the conductivity of some of these solutions have already been made, and some analyses of the solid compounds obtained in a few typical instances have already been published (this vol., 919).

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CXIII.—*Some Compounds of Aluminium Chloride with Organic Substances containing Oxygen.*

By JAMES WALLACE WALKER and ARTHUR SPENCER.

It has been shown by various investigators that the halogen compounds of aluminium have a great tendency to combine directly with many substances containing oxygen. The existence of several of these has been indicated in different ways during the Friedel-Crafts reaction. Gattermann (*Ber.*, 1892, 25, 3522 and 3531) noticed the formation of such compounds with *o*-nitrotoluene and anisole; and more recently a considerable number of compounds with the acyl chlorides and the ketones—the intermediate and the final products of the Friedel-Crafts ketone synthesis—have been examined by Boeseken (*Abstr.*, 1900, 78, i, 349) and by Kohler (*Amer. Chem. J.*, 1901, 24, 385). All of them seem to contain one molecular proportion of the organic constituent referred to the formula  $AlX_3$ . In connection with the work described in the two preceding communications (this vol., 1082 and 1098) it seemed of interest to examine a few more cases in which aluminium chloride dissolves in oxygen compounds, especially those containing more than one atom of oxygen. In the following experiments the aluminium chloride was brought into contact with an excess of the organic reagent dissolved in carbon disulphide, as the reaction was in many instances too violent to perform without a diluent, and as otherwise the high boiling points of many of the organic substances would have prevented the purification of the product by evaporating off any excess of the volatile reagent. This procedure, although regrettable, since it gives but little indication of the condition in which such compounds would crystallise from an excess of the organic reagent, seemed, however, to be unavoidable.

*Aluminium Chloride and Ether.*—The compound obtained in the manner just described, which floated as a yellow oil on the surface of the carbon disulphide, was separated, and the excess of solvent evaporated in a current of dry air. It crystallised in large, brown plates. Two estimations of aluminium made with different preparations gave 13.92 and 13.94 per cent., instead of 13.01 per cent. calculated from the formula  $C_4H_{10}O, AlCl_3$ . Since aluminium chloride had been found to yield a solution of slight conductivity when dissolved in anisole (*loc. cit.*), it was thought advisable to test the ethereal solution in the same way, as Kahlenberg and Lincoln had found (*J. Physical Chem.*, 1899, 3, 19) no conductivity for a solution of ferric chloride in ether although that salt when dissolved in anisole showed a slight conducting power. Freshly prepared aluminium

chloride was employed for the purpose, 0.1876 gram being distilled directly into the conductivity cell and dissolved in 5 c.c. of ether which had been dried for some time over sodium. The result shows that it is only a feeble ionising medium for aluminium chloride, although somewhat better than anisole. It is probable that had acetyl or benzoyl chloride been added to it the conductivity would have been higher:  $V = 3.58$ ;  $\mu = 0.09$  at  $18^\circ$ .

*Aluminium Chloride and Anisole.*—This compound was obtained in very large, pink crystals by evaporation of the whole carbon disulphide solution, in which it was quite soluble. These crystals were broken up, washed with more carbon disulphide, and freed from adhering solvent by a current of dry air. An estimation of aluminium showed that the compound has the composition represented by the formula  $C_7H_8O, AlCl_3$ , since it yielded 11.23 per cent. instead of the theoretical 11.18 per cent.

Although aluminium chloride dissolves readily in phenetole an additive compound was not obtained in a crystalline condition. These compounds are of interest as representing oxonium compounds of the ethers, or at least compounds in which the valency of the oxygen atom is higher than two.

The behaviour of a few substances containing more than one oxygen atom was next examined to determine whether there is a proportionality between the number of atoms of oxygen present and of molecules of aluminium chloride combined. As in some instances the compound formed was a solid which did not seem to be at all soluble in carbon disulphide, it was necessary to triturate the solid with the solution. This was done, of course, in such a way as to exclude moisture.

*Aluminium Chloride and Ethyl Benzoate.*—The compound crystallised at once from the cold solution in white, feathery crystals. After washing and drying it was found to contain 9.85 per cent. of aluminium, whilst the formula  $C_9H_{10}O_2, AlCl_3$  requires 9.52 per cent.

*Aluminium Chloride and Methyl Mandelate.*—When the solution of methyl mandelate in carbon disulphide was added to the aluminium chloride, the latter slowly changed colour without dissolving and assumed a waxy consistency. Subsequently, when well washed with carbon disulphide, it was a pale yellow, granular powder. On analysis it yielded 16.10 per cent. of aluminium, whilst the formula  $C_9H_{10}O_3, 4AlCl_3$  requires 16.33 per cent.

*Aluminium Chloride and Ethyl Oxalate.*—On mixing these substances and warming slightly, a heavy, yellow liquid separated from the carbon disulphide. After repeated washing, and drying in a current of dry air, it formed a flocculent, white powder which was found to contain 9.45 per cent. of aluminium instead of 9.66 per cent. required by the formula  $C_6H_{10}O_4, AlCl_3$ .

*Aluminium Chloride and Ethyl Malonate.*—The aluminium chloride was in this instance converted into a clear, yellow, viscous substance. After washing and drying in the usual way, it yielded on analysis 8·73 per cent. of aluminium, while the formula  $C_7H_{12}O_4, AlCl_3$  requires 9·20 per cent. Many of the results were checked by analyses of material taken from different preparations. The aluminium only was estimated, as this was considered sufficient to discriminate between one, two, or more molecular ratios of aluminium chloride.

*Aluminium Chloride and Acetic Acid.*—The aluminium chloride became at first soft and sticky, but after rubbing for some time in the liquid it formed yellow, granular particles. Analyses showed that the product contained 18·04 per cent. of aluminium, which approximates very closely to that which is required by the formula  $C_2H_4O_2, 4AlCl_3$ , namely, 18·18 per cent.

*Aluminium Chloride and o-Nitrotoluene.*—The compound was in this instance quite soluble in warm carbon disulphide containing a slight excess of o-nitrotoluene, and crystallised out in yellow crystals on cooling. After washing and drying it was found to contain 10·31 per cent. of aluminium, instead of 9·98 per cent. required by the formula  $C_7H_7O_2N, AlCl_3$ .

*Aluminium Chloride and m-Dinitrobenzene.*—The product in this reaction was semi-solid when cold, but melted on gentle warming to a clear liquid. It was thus easily separated from excess of aluminium chloride. Although repeatedly washed with carbon disulphide, however, separation from excess of organic material was evidently more difficult than in previous cases, as the substance yielded on analysis 7·93 per cent. of aluminium, instead of 8·95 per cent. required by the formula  $C_6H_4O_4N_2, AlCl_3$ . These results are tabulated below:

Substance used.	Probable formula of compound.		Theoretical percentage of Al.	Percentage found.
Ether .....	$(C_2H_5)_2O$	$AlCl_3$	13·01	13·93
Anisole ... ..	$CH_3 \cdot O \cdot C_6H_5$	$AlCl_3$	11·18	11·23
Ethyl benzoate .....	$C_6H_5 \cdot CO_2 \cdot C_2H_5$	$AlCl_3$	9·52	9·85
Methyl mandelate.....	$C_6H_5 \cdot CH(OH) \cdot CO_2 \cdot CH_3$	$4AlCl_3$	16·33	16·10
Ethyl oxalate.....	$(CO_2 \cdot C_2H_5)_2$	$AlCl_3$	9·66	9·45
Ethyl malonate .....	$CH_2 \cdot (CO_2 \cdot C_2H_5)_2$	$AlCl_3$	9·20	8·73
Acetic acid.. ..	$CH_3 \cdot CO_2H$	$4AlCl_3$	18·18	18·04
o-Nitrotoluene .....	$CH_3 \cdot C_6H_4 \cdot NO_2$	$AlCl_3$	9·98	10·31
m-Dinitrobenzene .....	$C_6H_4(NO_2)_2$	$AlCl_3$	8·95	7·93

There is apparently no connection between the number of atoms in the molecule of the substance and the number of molecules of aluminium chloride with which it can combine. It seems also as if under certain conditions the valency of the oxygen atom may be greater than four, as in the compounds with methyl mandelate and

acetic acid, unless, of course, we assume that there is a molecule of aluminium chloride attached to each atom of oxygen.

Kohler (*loc. cit.*) determined the molecular weights in carbon disulphide solution of a number of the compounds of aluminium chloride and bromide with the acyl chlorides, the ketones, and the nitrohydrocarbons, and found that they consisted of double molecules. Hence he concludes that the formula for aluminium chloride in solution is  $\text{Al}_2\text{Cl}_6$ , even although a determination in nitrobenzene gave the formula  $\text{AlCl}_3$ , and although Werner obtained the latter result also in pyridine solution. The reason given for this conclusion is, that since the compound of aluminium bromide and benzoyl chloride when dissolved in nitrobenzene gives a molecular weight of 370 instead of at least 407.5, it is impossible to determine molecular weights in a solvent with which the solute combines. Very probably, however, in this instance the nitrobenzene partially displaces the benzoyl chloride from its compound.

Having prepared the compound of *o*-nitrotoluene with aluminium chloride, we attempted to determine its molecular weight in that liquid as solvent by measurement of the depression of the freezing point. In purifying Kahlbaum's purest material, which solidified at  $-10^\circ$ , for this purpose, the liquid was continuously stirred during the process of freezing. It was observed that, after a considerable quantity had frozen out, the temperature suddenly began to rise. It rose rapidly until it reached  $-4.25^\circ$ , at which point it remained stationary till all had solidified. The less fusible crystals seemed denser and more gritty than the more fusible. Thinking that an impurity might be present, we prepared a considerable quantity of the substance freezing at  $-4.25^\circ$ , but this, when cooled in the liquid condition below  $-10^\circ$ , showed exactly the same behaviour as the original, and the liquid from which it had been separated by crystallisation behaved likewise. By repeated recrystallisation we could not obtain any fraction which did not exhibit both freezing points. Nitrotoluene must therefore be dimorphous, in this respect resembling *m*-chloronitrobenzene. As no data regarding the molecular lowering of the freezing point or the latent heat of liquefaction of *o*-nitrotoluene could be found, benzene was employed in order to determine the lowering of the freezing point of the modification melting at  $-4.25^\circ$ , with the following results:

Solvent.	Benzene.	Depression.	Molecular depression.
19.787 grams	0.0516 gram	0.23°	69
19.787    ,,	0.1516    ,,	0.63	65
23.187    ,,	0.3868    ,,	1.31	61
23.187    ,,	0.5013    ,,	1.55	56

These values point to a molecular depression at zero concentration of 72, or almost the same as that for nitrobenzene, namely, 70. Attempts were made to determine the corresponding value for the modification melting at  $-10^{\circ}$ , but, although the freezing point of the pure solvent could be accurately observed, it was found impossible to obtain a freezing point for this modification when a little benzene had been added to it. When even a very dilute solution was cooled below  $-10.5^{\circ}$  and a crystal of the more fusible modification added, the temperature would rise slowly to about  $-10.5^{\circ}$ , but without pause would then rise more rapidly to the higher freezing point. Evidently the addition of benzene renders the more fusible modification still more unstable. In a pure condition, when allowed to remain at rest the more fusible modification can be preserved indefinitely. Two determinations of the molecular weight of the compound with aluminium chloride were then made :

Solvent.	Compound.	Depression.	Mol. wt.
18.085 grams	0.4036 gram	$0.23^{\circ}$	700
18.085 „	0.6766 „	$0.415$	650

Since the molecular weight corresponding with the formula  $C_7H_7 \cdot NO_2 \cdot AlCl_3$  is 270.5, this result points to a high degree of association even in a 2 per cent. solution. There is an indication that the molecular weight falls as the concentration rises, as was found by Kahlenberg and Lincoln (*J. Physical Chem.*, 1899, 3, 19) for the similar case of ferric chloride in nitrobenzene, but in this case the difference of the two observations is not very striking. However, an attempted determination with a more dilute solution, namely, 0.58 per cent., gave no observable depression whatever with a Beckmann thermometer, whilst with a molecular weight of 700 it ought to have shown about  $0.06^{\circ}$ . This observation is interesting when taken in connection with that described in a preceding communication (this vol., p. 1087) regarding the conductivity of this same compound in *o*-nitrotoluene. Although the molecular conductivity at first increases with dilution after a certain point has been reached, it diminishes very rapidly with further increase in volume. This phenomenon was ascribed to the presence of moisture, but it is a point requiring further investigation.

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# CXIV.—*A Method for the Rapid Ultimate Analysis of Certain Organic Compounds.*

By JOHN NORMAN COLLIE.

THE method described in the following communication is not a new one, but a modification of that first suggested by Saussure and Prout. In 1827, Prout published a paper on organic analysis in the *Philosophical Transactions*, in which he described an apparatus for estimating the amount of carbon and hydrogen in an organic compound by the combustion of a known weight of the substance in a known volume of oxygen. Considering the difficulty of obtaining apparatus in those days, many of his results were marvellously accurate.

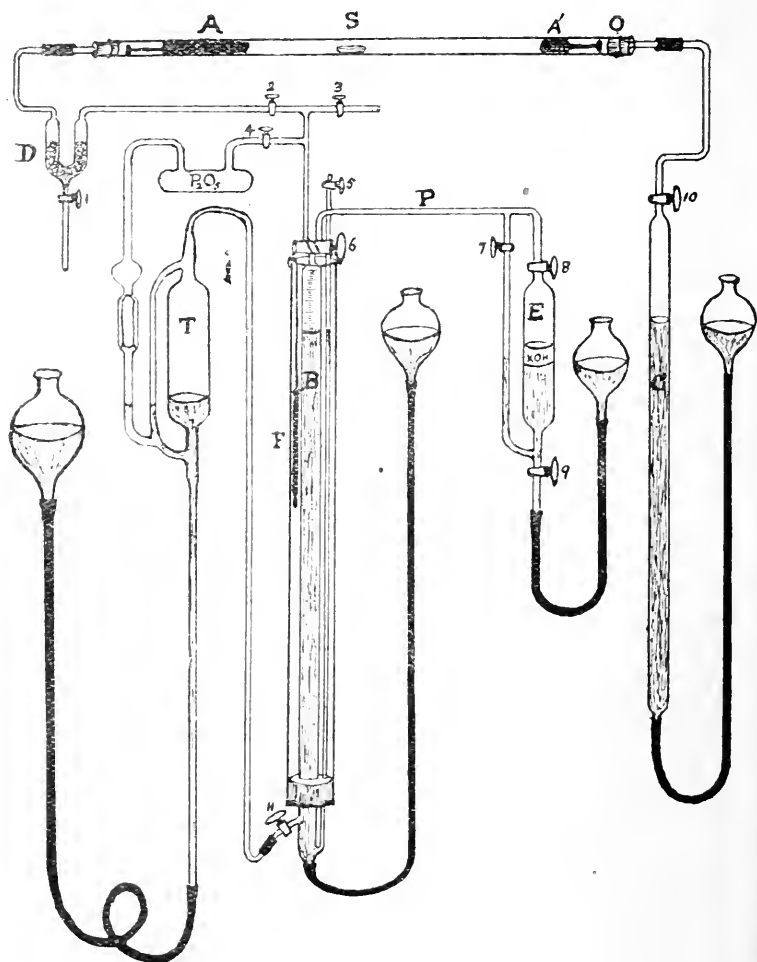
Nowadays, with mercury pumps, glass taps, and all the appliances of a modern laboratory, the method should at least not be less accurate, and at the same time should be far easier to carry out. It seemed therefore worth while to use this method again with such modifications as were possible, for the following reasons: (1) as it depends on measurements of volumes of gases, it is extremely accurate; (2) the amount of substance used can be reduced to nearly one-tenth of that ordinarily employed; (3) the time taken in an analysis ought to be very materially shortened.

At present, however, the method has its limitations, as it can only be used for the combustion of compounds containing carbon and hydrogen, or carbon, hydrogen, and oxygen, moreover, only for those which are not appreciably volatile in a vacuum.

An accurately weighed amount of the substance is introduced into a hard glass combustion tube, which can be heated in a furnace. The tube is filled with oxygen, the volume of which is obtained by exhausting the apparatus by means of a mercury pump and delivering the oxygen into a measuring tube. The oxygen is then allowed to re-enter the combustion tube, which is forthwith rapidly heated to redness, and even if complete combustion of the compound does not occur at once, the gases can be passed backwards and forwards through the tube by means of two mercury reservoirs, and any carbon monoxide is completely and rapidly burnt to carbon dioxide. The whole of the gases are pumped out again, measured, and passed into a separate vessel containing strong caustic potash solution to absorb the carbon dioxide, and finally back again into the measuring vessel. From the data obtained, the percentage of carbon and hydrogen in the compound can be calculated.

*Description of the Apparatus.*

A carefully weighed quantity of the substance to be analysed is introduced in a boat, *S*, into the combustion tube at *O*. The mercury pump, *T'*, is cleared of air by closing the tap 4 and delivering all the air



through the tap 11 into *B*. The mercury in *B* is then raised until all the air has been expelled; the tap 6 is then closed. Oxygen is passed into the combustion tube through the taps 3 and 4, and the displaced air allowed to escape by removing the core of tap 10, the mercury in the

reservoir, *C*, being brought to the level of tap 10. As soon as oxygen issues from the combustion tube, the core of tap 10 is replaced. Tap 3 is now closed, and the whole of the oxygen is allowed to enter the mercury pump by opening the tap 4. The volume is then read under atmospheric pressure, and the temperature of the water in the outer jacket surrounding the measuring tube, *B*, is noted on the thermometer, *F*. The height of the barometer is also taken. Tap 4 is now closed, and tap 6 is opened so that the oxygen may again enter the combustion tube.

The combustion tube may now be heated at *A* and *A'*, where asbestos, covered with copper oxide made from pure copper nitrate,\* is placed. As soon as both ends of the tube are red hot, all the burners under the combustion tube may be lighted, and the substance in the boat, *S*, volatilised as rapidly as possible. When this occurs, the tap 6 is slightly opened so as to draw the vapour of the substance mixed with oxygen over the red hot asbestos and copper oxides. Taps 6 and 10 are then fully opened, and the mercury in *B* and *C* rapidly raised and lowered alternately for two or three minutes. Most of the water produced by the combustion of the compound is absorbed in tube *D*, which is filled with pumice moistened with sulphuric acid. This sulphuric acid can be renewed by allowing it to run out through tap 1 and afterwards sucking up a fresh supply.

The actual combustion of the substance should take less than five minutes, and from the results obtained seems to be very complete.

The mercury in *B* is now raised to tap 6, which is closed. Tap 4 is slowly opened, so that the gas before entering the pump may be dried by passing, not too quickly, over the phosphoric anhydride. As soon as the mercury in *C* has risen to the tap 10, this should be closed, otherwise mercury will run into the combustion tube. The whole of the gas in the apparatus can now be pumped into the measuring tube, *B*. It is safest, perhaps, to allow the gas again to stream slowly into the pump by closing tap 4 and opening tap 6, the reason for this being that even a small amount of moisture makes a considerable difference in the volume. After delivering the gas again into *B*, its volume can be read.

To absorb the carbon dioxide, the gas is now transferred to the vessel *E*, through the tube *P*, which should be of capillary bore. By raising and lowering the reservoir in connection with *E*, the carbon dioxide is very soon absorbed and the residual gas is then returned to *B*. At this point also it is best to send the gas once through the pump, over

\* An attempt was made to produce pure copper oxide by heating a spiral of very thin copper gauze. First it was heated for five hours in a current of air, then for over two days in oxygen gas; even after this treatment it still slowly absorbed oxygen.

the phosphoric anhydride, in order to remove traces of moisture. The volume of the gas is now measured for the last time.

The author has completed such a combustion in thirty-five minutes, but as a rule the time employed should be about one hour, for too much haste may easily ruin, not only the analysis, but also the apparatus. For instance, if the gas be allowed suddenly to enter the mercury pump through the tap 4, while mercury is in the head of the pump, it will drive the liquid before it with such violence that the top of the pump is certain to be broken.

### *Results of Analyses.*

The first substance employed to test the apparatus was  $\beta$ -naphthol.

$\beta$ -Naphthol taken, 0.0163 gram; oxygen in apparatus, 107.3 c.c.; gas after combustion, 103.5 c.c.; gas after absorbing  $\text{CO}_2$ , 78.4 c.c. In every case the volume is reduced to N.T.P. From these results, the following data can be obtained: diminution due to the production of water by the oxygen, 3.8 c.c.; diminution due to the production of carbon dioxide, 25.1 c.c. Amount of carbon = 0.013554 gram, whence C = 83.2 per cent.

The percentage of hydrogen can be determined indirectly, inasmuch as part of the hydrogen *a* in the substance is oxidised by means of the oxygen in the tube, and part *b* is oxidised to water by means of the oxygen already in the compound.

The weight of part *a* can be calculated as follows: the diminution in volume after combustion = 3.8 c.c. This is due entirely to oxygen consumed to form water (for the oxygen employed in forming carbon dioxide produces its own volume of carbon dioxide). Therefore 3.8 c.c. will have combined with 7.6 c.c. of hydrogen.

$a$  = weight of 7.6 c.c. of hydrogen = 0.000684 gram.

The weight of part *b* is found in the following manner: weight of substance taken = weight of carbon and hydrogen found + weight of water produced by the combined oxygen in the substance.  $0.0163 - (0.013554 + 0.000684) = 0.002062$  (weight of water), which is equivalent to 0.000229 gram of hydrogen. Hence the total hydrogen is  $0.000229 + 0.000684 = 0.000913$  gram, the percentage being 5.6.

Two more combustions were made.

	Found.		Calculated.
			$\text{C}_{10}\text{H}_8\text{O}$ .
C	83.3	83.0	83.3
H	5.3	5.2	5.5

Several other substances were analysed; the amounts taken were never more than 0.04 or less than 0.012 gram.

*Dimethylpyrone, C<sub>7</sub>H<sub>8</sub>O<sub>2</sub>.*

	I.	II.	III.	Calculated.
C.....	67.7	67.4	67.9	67.8
H .....	6.4	6.9	6.7	6.4

*Cane Sugar, C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>.*

	I.	II.	III.	IV.	Calculated.
C .....	42.3	42.4	42.0	42.3	42.1
H .....	6.7	6.2	6.5	6.1	6.4

*Diacetyldimethylpyrone, C<sub>11</sub>H<sub>12</sub>O<sub>4</sub>.*

	I.	II.	Calculated.
C.....	63.1	63.2	63.5
H .....	6.1	5.5	5.8

*Anthracene, C<sub>14</sub>H<sub>10</sub>.*

	I.	II.	III.	Calculated.
C.....	94.1	94.4	93.9	94.4
H .....	5.6	5.5	5.8	5.6

*Phthalic Anhydride, C<sub>8</sub>H<sub>4</sub>O<sub>3</sub>.*

	I.	II.	Calculated.
C.....	65.1	64.7	64.8
H .....	3.1	2.4	2.7

The errors of experiment in this method for the ultimate analysis of organic compounds are not great. The substance can be accurately weighed to tenths of a milligram, an error therefore of one-tenth of a milligram in 0.030 gram of substance is only one in three hundred. In reading the volume of carbon dioxide (as a rule, the amount produced is from 40—50 c.c.), the error is probably not more than a tenth of a c.c.; here again the error would only be about one in four hundred. Of course, however, any error in the amount of carbon also affects the hydrogen, and should the percentage of carbon be too high, then the hydrogen would probably be too low, and *vice versa*. Incomplete combustion of the substance, as a rule, only occurs in one way, namely, by the partial burning and subsequent condensation of difficultly volatile compounds on the tubes between the combustion tube and the rest of the apparatus. This, however, does not occur

when asbestos mixed with copper oxide is present in the combustion tube.

When once the apparatus has been fitted up, it is merely necessary to weigh out the substance in a boat, take out the india-rubber cork at *O*, and put the boat into the combustion tube. As it does not matter whether the tube is moist or not, the india-rubber cork can be wetted before it is replaced, and by that means a perfectly tight joint results. Three combustions can be easily made in an afternoon, and the total amount of substance used need only be 0.10 of a gram.

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CXV.—*The Influence of Solvents on the Rotation of Optically Active Compounds. Part V. The Optical Activity of Certain Tartrates in Aqueous Solution.*

By THOMAS STEWART PATTERSON.

ALTHOUGH the data relative to the rotation values of optically active compounds have greatly accumulated during the past ten or twenty years, it must nevertheless be admitted that the numbers obtained serve chiefly to show how complicated is the problem under investigation. Very few regularities are known, which can claim to be in any sense general, and we have learned merely that external influences such as the temperature, the nature of the solvent, the refrangibility of the light used, and probably also the pressure must all be carefully studied before the connection between rotation value and chemical constitution can be regarded as being more than purely empirical. The chief difficulty seems to lie in the fact that we have little or no means of judging as to when different active substances are in such conditions that their rotation constants are really comparable, and it therefore becomes of very great importance to study, not merely isolated rotation values of different compounds, but rather the variation which rotation is capable of undergoing with alteration of external conditions. Several researches (Trans., 1901, 79, 167 and 477; 1902, 81, 1097 and 1134) have been undertaken with this object, and the present paper is an account of further work in a slightly different direction.

Aqueous solutions of the sodium, potassium, potassium methyl,

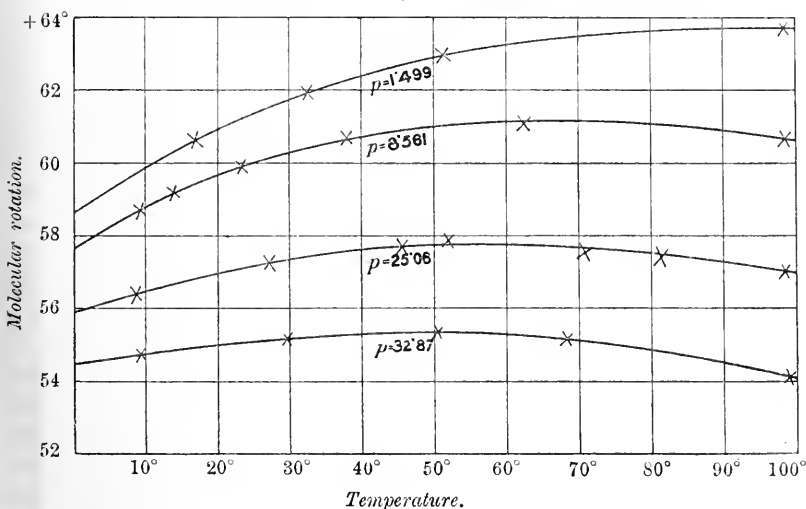
potassium ethyl, potassium *n*-propyl, methyl, ethyl, and *n*-propyl salts of tartaric acid have been examined at several concentrations and at a number of different temperatures with the object of discovering: (1) the effect of temperature-change in each case; (2) whether the relationships amongst the data for the alkyl tartrates are simpler in dilute aqueous solution than in the homogeneous condition; (3) whether any connection can be established between the rotation of the tartaryl ion, the three alkyl-tartaryl ions, and the undissociated molecules of the three alkyl tartrates, all in dilute aqueous solution.

The data obtained in the investigation of the foregoing substances will be found collected together at the end of the paper, whilst the general results are shown by the various curves. The strengths (*p*) of the solutions represent grams of anhydrous substance per 100 grams of solution.

### *Optical Behaviour of the Compounds Examined.*

*Sodium Tartrate.*—The results obtained in the examination of this salt are shown in Fig. 1, which represents the dependence of mole-

FIG. 1.—Molecular rotation of aqueous solutions of sodium tartrate.



cular rotation on concentration and temperature, but is reproduced chiefly on account of the temperature effect, which in all the solutions dealt with in this investigation is of very considerable interest.

Six solutions of sodium tartrate were examined, but in two cases the observations did not extend over any great range of temperature, and therefore only four curves are shown.

In the most dilute solution ( $p=1.5$ ) it will be noticed that the molecular rotation gradually increases as the temperature rises, but more rapidly at low temperatures than at higher ones, and since in this solution we may assume the substance to be nearly completely dissociated, this curve practically represents the effect of change of temperature on the tartaryl ion in aqueous solution. The next curve ( $p=8.56$ ) shows a generally similar behaviour, but here the rotation reaches a maximum value ( $+61.15^\circ$ ), about  $67^\circ$ , and then diminishes slightly to  $+60.6^\circ$  at  $100^\circ$ . The curve for  $p=25.06$  is somewhat flatter; a maximum ( $+57.8^\circ$ ) is reached at  $55^\circ$ , and the subsequent diminution in rotation to  $+57^\circ$  at  $100^\circ$  is a little greater than before. In the solution having  $p=32.9$ , the maximum occurs at  $50^\circ$  and the diminution to  $100^\circ$  is  $1.2^\circ$ .

One of the most interesting points about these curves is the occurrence of maximum rotations, but, as will appear subsequently, this is by no means an uncommon phenomenon, and its discussion may be meantime deferred (see p. 1135).

From the curves of Fig. 1 and the data on p. 1143 we find by interpolation the following numbers:

$p$ .	$[M]_D^{20^\circ}$ .	$[M]_D^{100^\circ}$ .	$p$ .	$[M]_D^{20^\circ}$ .	$[M]_D^{100^\circ}$ .
1.499	$+60.90^\circ$	$+63.73^\circ$	25.06	$+56.98^\circ$	$+57.00^\circ$
4.154	60.05	—	32.873	54.98	54.10
8.561	59.66	60.60	49.35	—	46.27

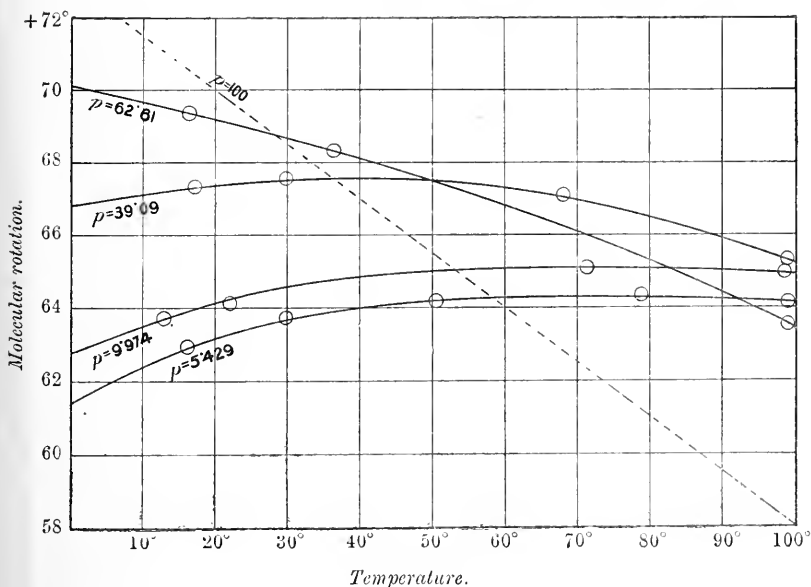
From these values, the two curves for sodium tartrate shown in Fig. 3 have been obtained. One of these represents the behaviour of this substance on dilution at  $20^\circ$ , from which it would appear that the tartaryl ion has a greater rotation than undissociated sodium tartrate. By extrapolating to zero concentration, the rotation of the tartaryl ion is found to be very nearly  $+61.5^\circ$ , and by extrapolating in the opposite direction, which is very much less accurate, the homogeneous salt would appear to have a molecular rotation of about  $+15^\circ$ .

The second curve for  $100^\circ$  is quite similar in character. Dilute solutions show a higher rotation at  $100^\circ$  than at  $20^\circ$ , but the difference between these values gradually diminishes, until at  $p=25$  the rotations at  $100^\circ$  and at  $20^\circ$  are the same. The curve for  $100^\circ$  then falls below that for  $20^\circ$ , from which it may be concluded that whilst the rotation of the ion increases with rise of temperature, the undissociated compound shows the opposite behaviour. By extrapolation, we find for  $p=0$ ,  $[M]_D^{100^\circ} = +63.5^\circ$ , and for  $p=100$ ,  $[M]_D^{100^\circ} = +10^\circ$  (approximately).

*Potassium Tartrate.*—In Fig. 2 (p. 1119), several of the temperature-rotation curves for potassium tartrate are shown. As regards the influence of temperature-change, the behaviour is, in general, similar to

that of sodium tartrate. The rotation of the most dilute solution ( $p=5.43$ ) increases by some  $3^\circ$  between  $0^\circ$  and  $100^\circ$ . When  $p=9.97$ , a maximum becomes apparent at about  $65^\circ$ , but is not very pronounced; for  $p=39.09$ , there is a maximum at  $40^\circ$ , whilst in the next solution ( $p=62.61$ ) the rotation continuously diminishes, so that the behaviour of a concentrated solution, in which we may suppose the influence of the undissociated compound to preponderate, is in striking contrast to that of the most dilute solution, which we may regard as representing the influence of temperature-change on the free ion. From these

FIG. 2.—Molecular rotation of aqueous solutions of potassium tartrate.



curves, and the data on p. 1144, we find by interpolation or extrapolation the following figures :

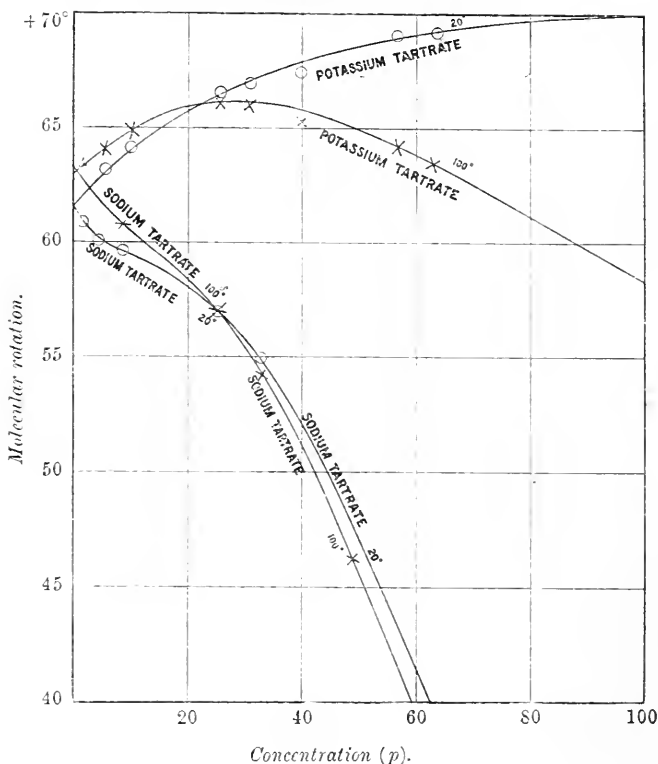
$p$ .	$[M]_D^{20^\circ}$ .	$[M]_D^{100^\circ}$ .	$p$ .	$[M]_D^{20^\circ}$ .	$[M]_D^{100^\circ}$ .
5.429	+63.20°	+64.10°	39.09	+67.40°	+65.25°
9.974	64.15	64.94	56.53	69.01	64.17
25.647	66.56	66.10	62.61	69.19	63.40
30.890	66.90	65.90			

The curves obtained from these data are shown in Fig. 3 (p. 1120). They represent a behaviour different from that of the sodium salt, for it will be noticed that at  $20^\circ$  the rotation increases steadily with increasing concentration, and, therefore, the rotation of undissociated potassium tartrate is greater than that of the tartarylion. By extrapolation

to  $p=0$ , we find, as might be expected, a value for the rotation of the ion practically identical with that obtained from the curve for the sodium salt; the value  $+61.5^\circ$ , to which both curves apparently tend, is certainly a close approximation to the truth, and is all the more trustworthy in that the two curves approach it from opposite directions.

On account of the greater solubility of the potassium salt, it is possible to examine strong solutions, and therefore extrapolation to

FIG. 3.—*Relationship between concentration and molecular rotation of sodium and potassium tartrates in aqueous solution.*



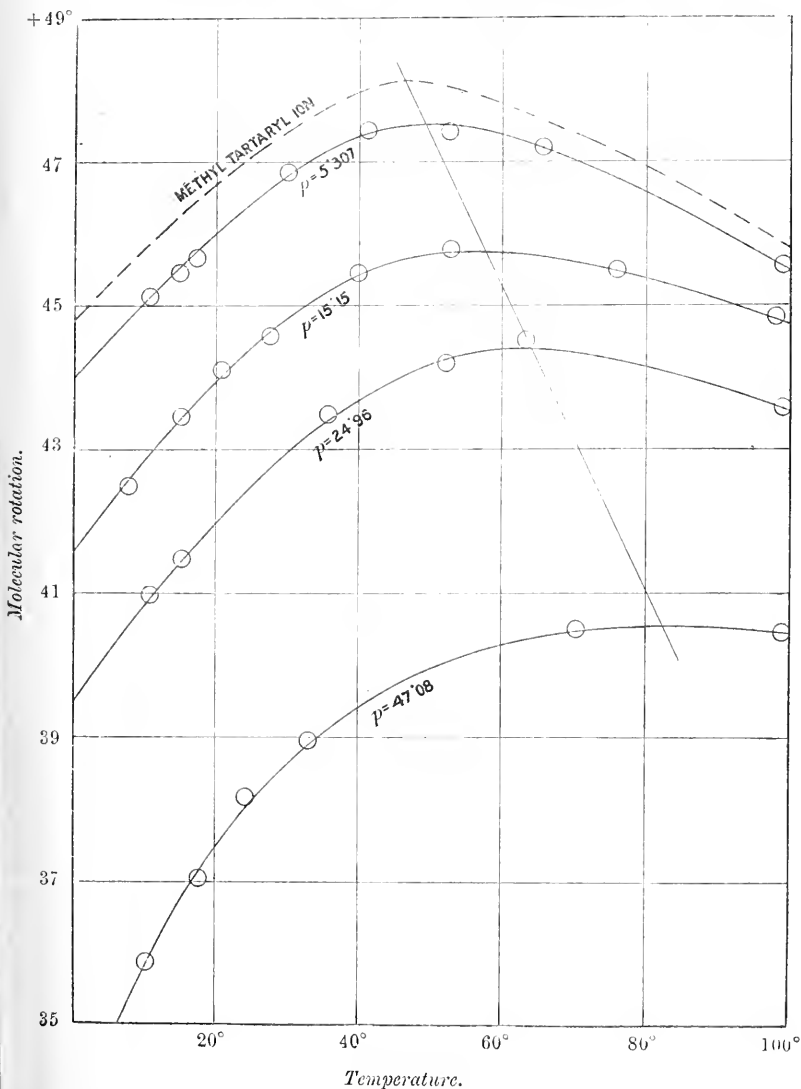
$p=100$  is fairly reliable. The value thus obtained for the homogeneous substance is  $[M]_D^{20} + 70^\circ$ , which is much greater than the corresponding rotation for the sodium salt.

The curve for  $100^\circ$  reaches a maximum value at about  $p=30$ . Extrapolation to  $p=0$  gives us in this case for the ionic rotation the value  $+63^\circ$ , which is close to that found from the curve for sodium tartrate ( $+63.5^\circ$ ). Taking the mean of the two values, we find  $+63.25^\circ$  as the rotation of the tartaryl ion at  $100^\circ$  in water at infinite

dilution, an estimate which is probably within 0.5 per cent. of the truth.

Extrapolating in the other direction, we find for the rotation of the

FIG. 4.—Molecular rotation of aqueous solutions of potassium methyl tartrate.



homogeneous salt at 100° the value +58°. The value at 20° was +70°, from which it appears that if homogeneous potassium tartrate

could exist in the liquid condition between  $20^{\circ}$  and  $100^{\circ}$  its rotation would rapidly diminish with rise of temperature in the manner shown by the broken line in Fig. 2.

*Potassium Methyl Tartrate.*—The influence of temperature-change on the rotation of solutions of potassium methyl tartrate is clearly shown by the curves in Fig. 4 (p. 1121).

In the most concentrated solution ( $p=47$ ), a maximum rotation probably occurs at  $82^{\circ}$ . The curve for  $p=25$  is similar, but here there is no doubt about the occurrence of a maximum rotation, which lies at or very near to  $64^{\circ}$ . For  $p=15.2$ , a distinct maximum rotation occurs at  $57^{\circ}$ . The curve for  $p=5.3$ , the most dilute solution examined, shows the same general characteristics, the maximum rotation being found at  $49^{\circ}$ .

By interpolation from the curves in Fig. 4, the following table is obtained:

$p$ .	$[M]_D^{20^{\circ}}$ .	$[M]_D^{100^{\circ}}$ .	$p$ .	$[M]_D^{20^{\circ}}$ .	$[M]_D^{100^{\circ}}$ .
5.3067	+45.99°	+45.50°	24.9555	+42.02°	+43.50°
15.1501	44.00	44.70	47.085	37.54	40.45

These data are plotted in Fig. 7. By extrapolation to  $p=0$ , the value found for the rotation of the methyl tartaryl ion is  $+46.7^{\circ}$  at  $20^{\circ}$ , and by extrapolation in the opposite direction the value  $[M]_D^{20^{\circ}} = +24.8^{\circ}$  is deduced for the superfused homogeneous salt.

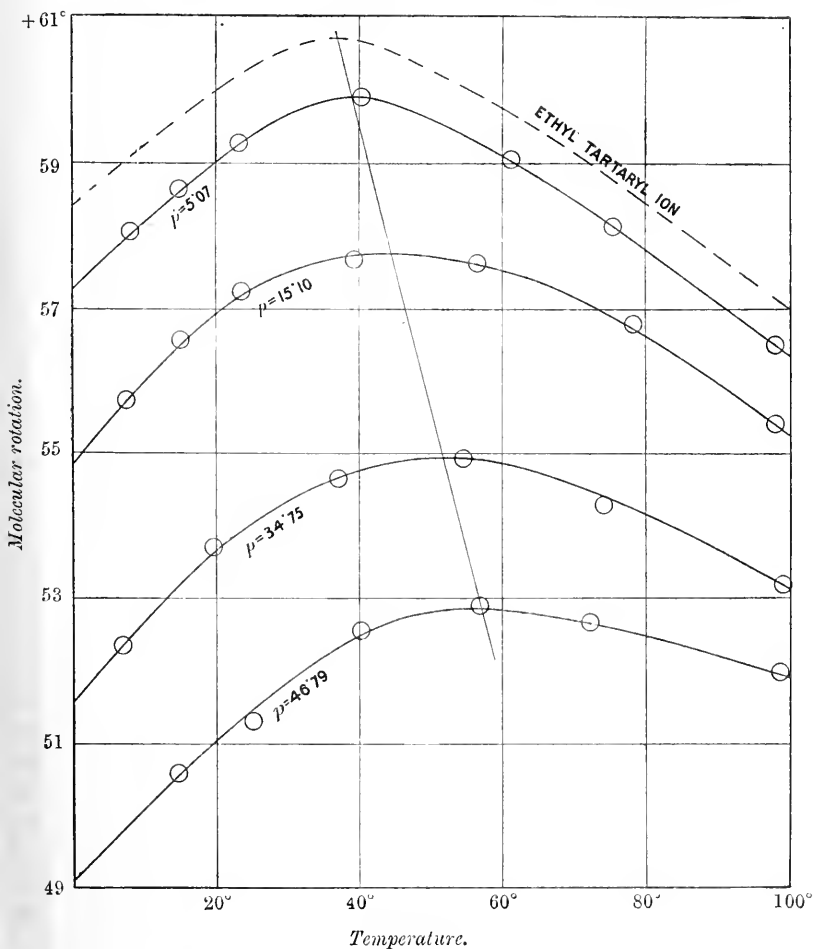
A similar examination of the curve for  $100^{\circ}$  gives  $+45.8^{\circ}$  for the rotation of the ion and  $+31.1^{\circ}$  for that of the homogeneous substance.

These data may be employed in obtaining the theoretical curve showing the influence of temperature-change on the ionic rotation. At  $20^{\circ}$ , this curve must pass through  $+46.7^{\circ}$ , and at  $100^{\circ}$  through the point  $+45.8^{\circ}$ . The other points on the curve may be found with sufficient exactitude by general appearance and from one other important criterion, namely, the occurrence of maximum rotations. These maxima are found at different temperatures according to the concentration of the solution, the maximum rotation being gradually displaced towards lower temperatures as the concentration diminishes, and it is of interest to notice that this displacement is very nearly a linear function of the concentration. This is shown by the fact that a straight line (see Fig. 4) may be drawn through the four maxima. By analogy, therefore, all the other maxima possible for solutions of intermediate concentration should lie along this line, which should thus also pass through the point of maximum rotation of the ion. From these considerations, the broken curve marked methyl tartaryl ion has been drawn. The maximum ionic rotation would occur at or near  $46.5^{\circ}$ , the corresponding rotation being  $+48.1^{\circ}$ .

*Potassium Ethyl Tartrate.*—The curves for this salt in Fig. 5 (p. 1123)

show the same general characteristics as those for potassium methyl tartrate, but some of the peculiarities noted in the behaviour of the latter are more pronounced, as will be seen by comparing the curves in pairs of corresponding concentrations.

FIG. 5.—Molecular rotation of aqueous solutions of potassium ethyl tartrate.



The rotation of the most dilute solution ( $p=5.07$ ) examined reaches a distinct maximum at  $38^\circ$ , the corresponding rotation being  $+59.95^\circ$ . For  $p=15.1$ , the maximum occurs at a temperature of  $46^\circ$ , the rotation being  $+57.74^\circ$ . A solution of  $p=34.75$  shows a maximum at  $53^\circ$ , when the rotation is  $+54.9^\circ$ , whilst in the last curve

a distinct maximum is still apparent at  $56^\circ$ , the rotation being  $+52.9^\circ$ . Since the maximum in the corresponding curve for potassium methyl tartrate has almost vanished, it would appear that the maximum rotation in solutions of potassium ethyl tartrate persists up to greater concentrations than in solutions of the former. In this case also the point of maximum rotation is displaced towards a lower temperature as the concentration diminishes, and this displacement is again linear, as is shown by the straight line passing through the four maxima. The maximum ionic rotation should therefore lie on this line.

The following table has been obtained by interpolation from the experimental data:

$p$ .	$[M]_D^{20^\circ}$ .	$[M]_D^{100^\circ}$ .	$p$ .	$[M]_D^{20^\circ}$ .	$[M]_D^{100^\circ}$ .
5.06845	$+59.06^\circ$	$+56.35^\circ$	34.747	$+53.68^\circ$	$+53.12^\circ$
15.1035	56.95	55.27	46.787	51.02	51.92

Fig. 7 (p. 1126) is obtained partly from these data, and by extrapolation to  $p=0$  the values obtained for the ethyl tartaryl ion are  $+60^\circ$  at  $20^\circ$ , and  $+57^\circ$  at  $100^\circ$ , whilst by extrapolation in the opposite direction we find for the superfused salt, if it could exist in this condition at these temperatures, the values  $+41.7^\circ$  at  $20^\circ$ , and  $+46.8^\circ$  at  $100^\circ$ . At lower concentrations, the curve for  $20^\circ$  lies above that for  $100^\circ$ , at higher concentrations, the reverse obtains.

The curve showing the behaviour of the ion with variation of temperature (Fig. 5) can be deduced from these data. It must pass through the points  $+60^\circ$  at  $20^\circ$  and  $+57^\circ$  at  $100^\circ$ , and the maximum rotation must lie on the line passing through the other maxima. The curve marked ethyl tartaryl ion has been obtained in this manner, and hence it may be concluded that the maximum ionic rotation occurs at  $37^\circ$  and has the value  $+60.7^\circ$ .

*Potassium n-Propyl Tartrate.*—The curves for this salt, which are shown in Fig. 6 (p. 1125), differ only in detail from those of Figs. 4 and 5. In the three solutions examined, the initial increase of rotation up to the maximum is not so rapid as in corresponding solutions of the other esters, whilst the subsequent diminution is more rapid. The maximum rotation is well marked in all three solutions, and again these points lie approximately along a straight line on which, presumably, the maximum ionic rotation should also fall.\*

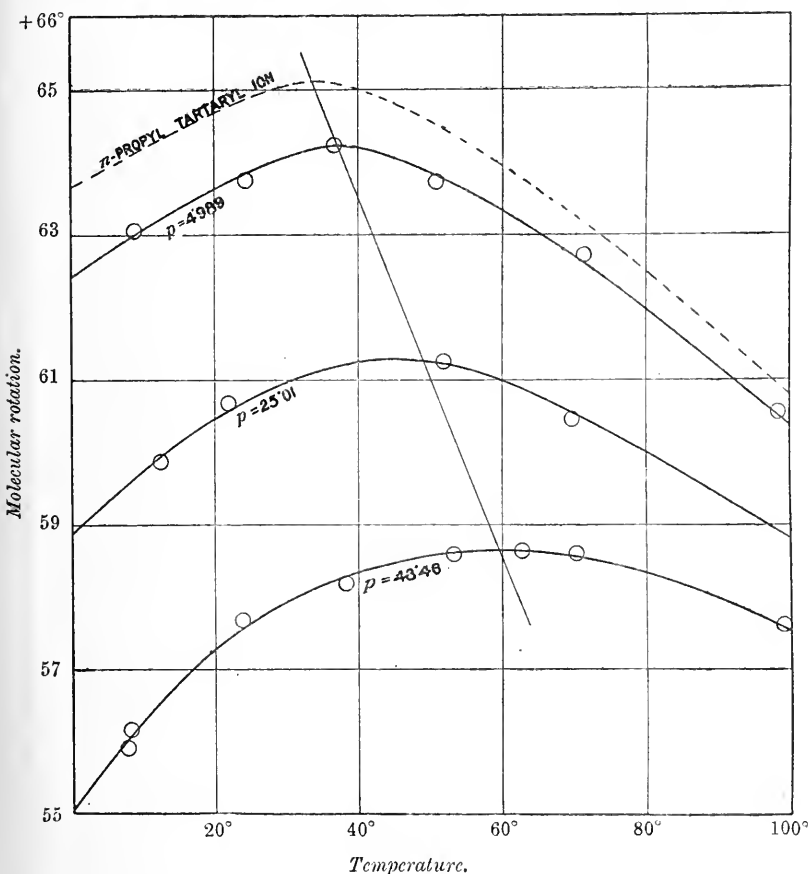
The data given in the following table are obtained from the three curves:

$p$ .	$[M]_D^{20^\circ}$ .	$[M]_D^{100^\circ}$ .
4.989	$+63.63^\circ$	$+60.40^\circ$
25.01	60.48	58.80
48.46	57.30	57.54

\* It was found somewhat difficult to purify this compound so as to obtain perfectly clear solutions for examination (see p. 1148). The results are therefore not quite so accurate as those for the other esters.

The concentration-rotation curves obtained from these data and shown in Fig. 7 may in the first place be compared with the curves given for the other two analogous esters. It will be noticed that variation of concentration produces the greatest effect on the rotation of the methyl ester, both at  $20^{\circ}$  and at  $100^{\circ}$ . In this respect the ethyl compound comes next, whilst the rotation of potassium *n*-propyl

FIG. 6.—Molecular rotation of aqueous solutions of potassium *n*-propyl tartrate.



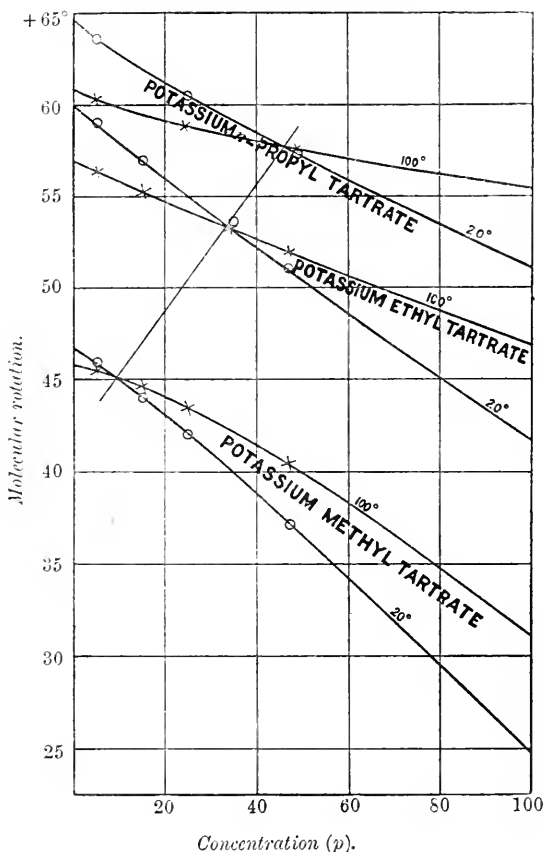
tartrate is least affected. In all three esters the effect of varying concentration is considerably less at  $100^{\circ}$  than at  $20^{\circ}$ , so that in the case of the *n*-propyl compound there is not much difference between the rotation of the homogeneous substance at  $100^{\circ}$ , and that of the ion at the same temperature.

The two concentration curves intersect one another at  $p = 45$ , and it

may be noticed that this and the corresponding points,  $p=27.3$  for the ethyl ester and  $p=10$  for the methyl ester, lie very nearly on the straight line shown in the diagram (Fig. 7).

By extrapolation of the two curves, the ionic rotations  $+64.7^\circ$  at  $20^\circ$  and  $+60.8^\circ$  at  $100^\circ$  are obtained, the rotations of the homogeneous

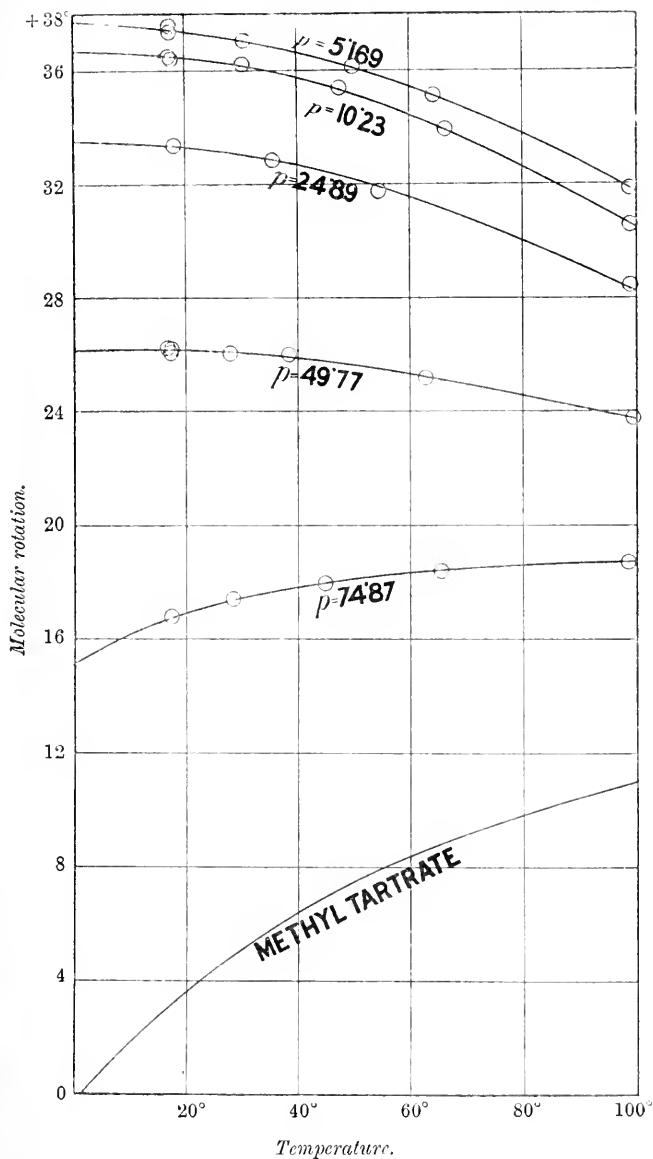
FIG. 7.—Relationship between concentration and molecular rotation of potassium alkyl tartrates at  $20^\circ$  and  $100^\circ$



salt being  $+51^\circ$  at  $20^\circ$  and  $+55.5^\circ$  at  $100^\circ$ . From these data and also from general appearance, the curve in Fig. 6 marked *n*-propyl tartaryl ion has been drawn, and it may be concluded that the maximum ionic rotation occurs at a temperature of  $34^\circ$ , and has the value  $+65.1^\circ$ .

*Methyl Tartrate.*—The experiments were carried out in this case in

FIG. 8.—Molecular rotation of aqueous solutions of methyl tartrate.



just the same way as with the other substances, although it might perhaps be expected that methyl tartrate, when heated with water at 100°, would undergo hydrolysis to such an extent as to vitiate the

results. The present experiments show, however, that in these circumstances, methyl tartrate undergoes very little decomposition.

In Fig. 8 (p. 1127), the various concentration-rotation curves obtained are shown. In the case of an ester, which can be examined in the homogeneous liquid condition, a more complete investigation of the rotation phenomena is possible than with the foregoing metallic salts, since the values for the homogeneous ester itself are known, so that there is less necessity for extrapolation.

The molecular rotation of methyl tartrate is small, being only  $+3.68^\circ$  at  $20^\circ$ , but it rises considerably on heating, reaching the value  $+11.00^\circ$  at  $100^\circ$ —an increase of  $7.32^\circ$ . The addition of a comparatively small quantity of water, so as to give a solution having  $p=75$ , has a very pronounced effect on the rotation, raising it by more than thirteen degrees to the value  $+16.8^\circ$  at  $20^\circ$ . At the same time, however, the influence of temperature-change becomes much less marked, the increase of rotation between  $20^\circ$  and  $100^\circ$  being only  $1.9^\circ$ . Further dilution to  $p=49.77$  brings about an increase in rotation to  $+26.2^\circ$ , and at this concentration an alteration in sign takes place in the influence of temperature-change, the rotation of this solution at  $100^\circ$  being  $+23.71^\circ$ . Further dilution increases the rotation at a somewhat diminishing rate, and, as the rotation increases, the temperature-coefficient becomes more distinctly negative. The behaviour of a dilute aqueous solution of methyl tartrate therefore presents a striking contrast to that of the homogeneous ester.

Interpolation from these curves gives the following table :

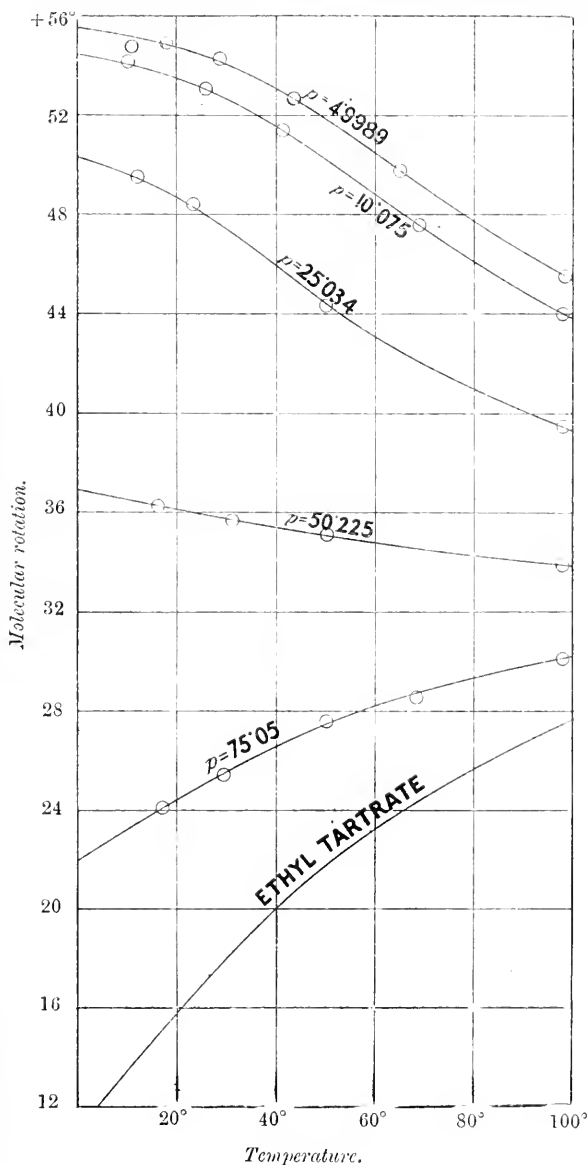
$p$ .	$[M]_D^{20^\circ}$ .	$[M]_D^{100^\circ}$ .	$p$ .	$[M]_D^{20^\circ}$ .	$[M]_D^{100^\circ}$ .
5.169	$+37.40^\circ$	$+31.72^\circ$	49.77	$+26.15^\circ$	$+23.71^\circ$
10.23	36.40	30.44	74.87	16.92	18.72
24.88	33.30	28.25	100.00	3.68	11.00

From these data, the concentration-rotation curves in Fig. 11 have been drawn. By extrapolation, the molecular rotations at infinite dilution are found to be  $+38.5^\circ$  at  $20^\circ$  and  $+32.2^\circ$  at  $100^\circ$ .

*Ethyl Tartrate.*—The data given in a former paper (Trans., 1901, 79, 171) regarding the optical behaviour of aqueous solutions of ethyl tartrate are unfortunately insufficient to allow of a satisfactory estimate of the rotations of the various solutions at  $100^\circ$ . The behaviour of ethyl tartrate has accordingly been re-examined.

The rotation-temperature curves are shown in Fig. 9 (p. 1129). They are, on the whole, similar to those for methyl tartrate, but there is one point of interest at least in which they differ, which could not have been observed from the previous results. It will be noticed that the curves for  $p=5$ ,  $p=10.08$ , and  $p=25.03$  at low temperatures, that is, between  $0^\circ$  and  $40^\circ$ , are concave to the horizontal axis. As the tempera-

FIG. 9.—Molecular rotation of aqueous solutions of ethyl tartrate.



ture rises, the rate of diminution of rotation increases. But at a certain temperature, which is higher the more dilute the solution, a change takes place, the curves become convex, the rate of diminution

of rotation becomes less, and the curves therefore show a point of inflection. As the concentration of the solutions increases, the initial concave part of the curve gradually disappears towards the left in such a way that the curve for  $p=50.2$  has, between  $0^\circ$  and  $100^\circ$ , only a convex appearance. The departure in these instances from the somewhat simpler shape of curve characteristic of methyl tartrate is but slight, and, had only one curve been examined, might well have been regarded as being due to experimental error, but since all four curves show an analogous behaviour, the more complex character of the ethyl tartrate curve must be admitted. This peculiar form is, however, only slightly marked in a solution with  $p=50.2$ , and it is therefore not surprising that for the more concentrated solution ( $p=75$ ) the curve bears a much closer resemblance to that for the homogeneous ester.

By interpolation from these curves, the following table is obtained:

$p$ .	$[M]_D^{20^\circ}$ .	$[M]_D^{100^\circ}$ .	$p$ .	$[M]_D^{20^\circ}$ .	$[M]_D^{100^\circ}$ .
5	+54.6°	+45.30°	50.225	+36.10°	+33.82°
10.08	53.5	43.80	75	24.40	30.15
25.03	48.73	39.30	100	15.78	27.75

It might naturally be expected that ethyl tartrate would be affected by solution in water in just the same manner as methyl tartrate, and that any difference observed would be of degree only. It has, however, just been pointed out that with regard to temperature-change in dilute solution the two esters do not behave quite similarly, and the curves in Fig. 11, drawn from the above data, show that both at  $20^\circ$  and at  $100^\circ$  there are also well-marked differences in the influence of varying concentration.

Similarly, it should be noticed that the two concentration curves for ethyl tartrate are not of the same shape, that for  $100^\circ$  resembling only one-half (from  $p=50$  to  $p=100$ ) of that for  $20^\circ$ .

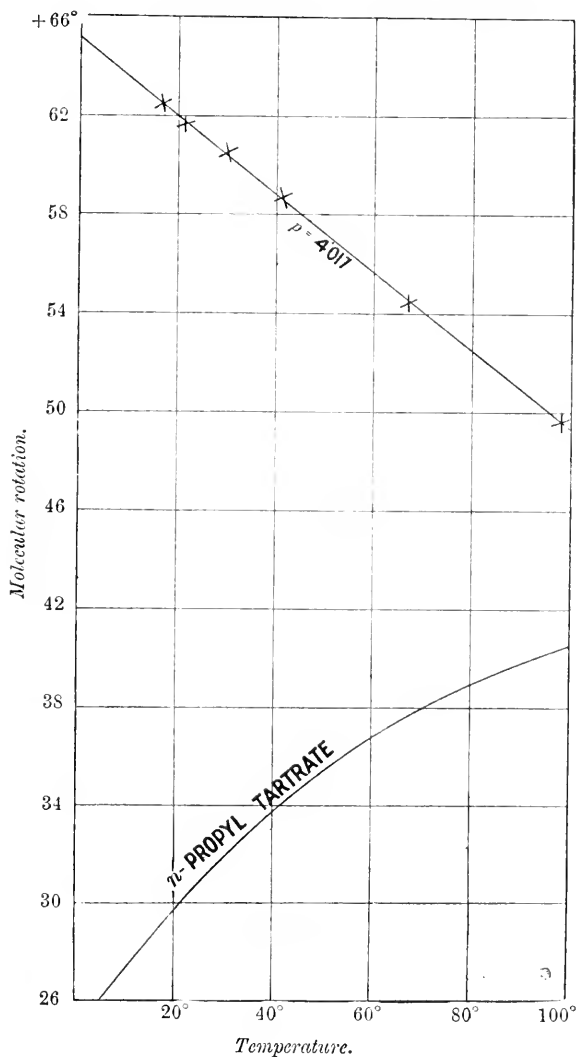
By extrapolation of these curves, the molecular rotation of ethyl tartrate at  $20^\circ$  appears to be very nearly  $+55.3^\circ$  at infinite dilution, whilst at  $100^\circ$  it has the value  $+46.8^\circ$ .

*n-Propyl Tartrate.*—On account of the fact that *n*-propyl tartrate is not miscible in all proportions with water, the observations made with it could not be so complete as with the other two esters. A preliminary trial showed that a solution of  $p=10$  (approximately) could be made in the cold, and the first solution examined was nearly of that strength. When the solution was heated to about  $30^\circ$ , however, it became milky and drops of *n*-propyl tartrate separated.\*

\* *n*-Propyl tartrate, therefore, becomes less soluble in water with rise of temperature, and may, in this connection, be employed in a lecture experiment. By shaking up water and the ester at the ordinary temperature for a few seconds and allowing to

It was impossible to determine the rotation of this solution above  $24^{\circ}$ , whilst the next, for which  $p = 6.99$ , just began to turn milky at  $77^{\circ}$ . A

FIG. 10.—*Molecular rotation of n-propyl tartrate.*



third solution,  $p = 7.006$ , was also examined, but, like the other two, only through a somewhat limited range of temperature. The most settle, an upper aqueous layer is obtained, which almost immediately becomes turbid if the tube be held in the hand or immersed in warm water.

important of the solutions of *n*-propyl tartrate investigated was that of  $p=4.017$ , since its rotation and density could be determined up to  $100^\circ$ .

The curves for this solution and the homogeneous ester are shown in Fig. 10 (p. 1131), the contrast between them being very striking. Whilst the rotation of the pure ester increases by some  $16^\circ$  between  $0^\circ$  and  $100^\circ$ , that of the dilute solution diminishes by an almost exactly equal amount; the line for the solution is straight, whilst that for the ester is curved; the rotation of the dilute solution at  $0^\circ$  is more than 2.5 times as great as that of the pure ester at the same temperature, whereas they would probably be almost equal at a temperature of  $130^\circ$ . It may also be noticed that in respect to temperature-change the dilute solution behaves somewhat differently from both methyl and ethyl tartrates, the curve being apparently a straight line.

Owing to the insolubility of the ester, it is in this case not possible to draw a complete concentration-rotation curve, which is unfortunate because, since dilution has different effects on methyl and ethyl tartrates, it would be most interesting to know how the rotation of *n*-propyl tartrate would be modified by the same cause.

The following data, obtained by interpolation from the experimental data, show the influence of concentration change so far as it could be determined in this case.

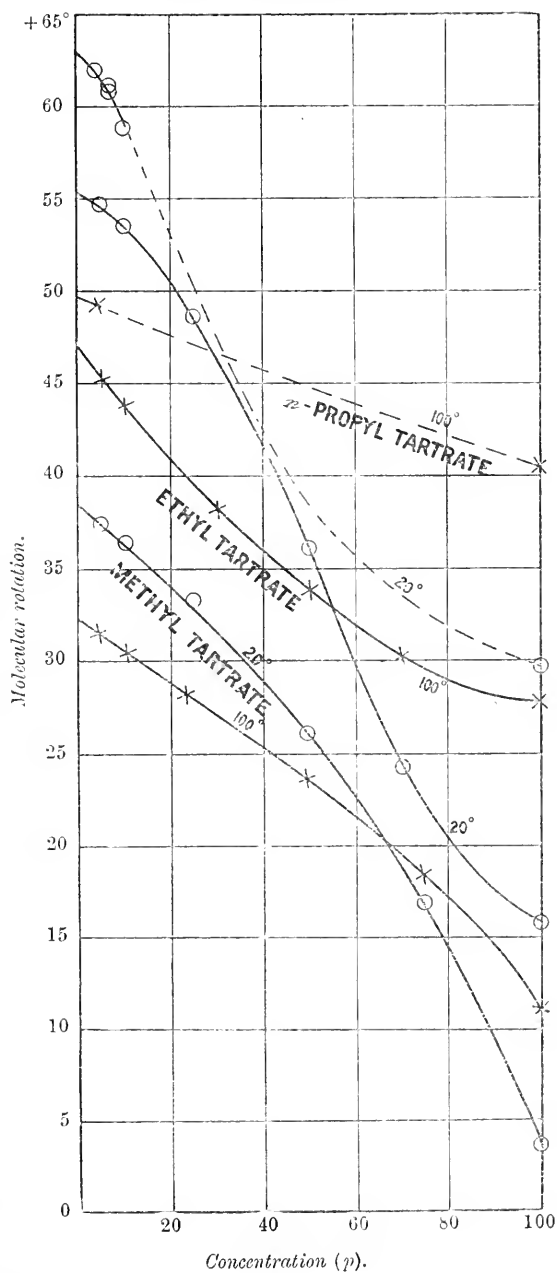
$p$ .	$[M]_D^{20^\circ}$ .	$[M]_D^{100^\circ}$ .	$p$ .	$[M]_D^{20^\circ}$ .	$[M]_D^{100^\circ}$ .
4.017	+62.01°	+49.3°	7.006	+60.79°	—
6.995	61.18	—	10.02	58.85	—

From the results obtained it would appear that the initial part of the curve for  $20^\circ$  resembles the initial part of the ethyl tartrate curve, and this in turn between  $p=0$  and  $p=50$  resembles the whole of the methyl tartrate curve, as will be seen from Fig. 11 (p. 1133). It is not possible to state exactly what the remainder of the *n*-propyl tartrate curve would be like, but it would probably resemble that for ethyl tartrate as shown by the broken line in Fig. 11.

By extrapolation, the molecular rotation at infinite dilution is found to be  $+63^\circ$  at  $20^\circ$  and  $+49.6^\circ$  at  $100^\circ$ .

#### *General Consideration of Results.*

That each of the three classes of compounds examined shows a characteristic behaviour, especially as regards the influence of temperature-change, is quite in agreement with the dissociation theory. It is to be expected that solutions of the three alkyl tartrates, containing undissociated molecules, would differ markedly from solutions of the potassium alkyl tartrates, but only in detail from each other, and that

FIG. 11.—*Relationship between concentration and molecular rotation of alkyl tartrates at 20° and 100°.*


both these series should in turn differ from sodium or potassium tartrate.

On the other hand, several facts may be noted which do not at first sight accord so well with the ionic theory. A reference to Figs. 3, 7, and 11 will show that, with one exception, all the compounds examined behave in the same manner with regard to variation in concentration. This exception is potassium tartrate, the rotation of which (at 20°) diminishes with dilution, whilst the rotations of all the other substances increase. It is not surprising that the concentration-rotation curves shown in Fig. 7 for the potassium alkyl tartrates should resemble each other, but it could scarcely have been expected that the curves in Fig. 11 for methyl tartrate should also be of very nearly the same type. This nevertheless is the case. The methyl tartrate curves bear, indeed, a greater likeness to the potassium alkyl tartrate curves than they do to those for ethyl tartrate.

Now the influence of dilution on methyl tartrate solutions must be ascribed to solvent action. It is almost certain that there is at least no ionic dissociation. But in potassium methyl tartrate, for instance, both ionic dissociation and solvent action are effective. It might therefore be imagined that, as dilution increases, the solvent action of the water, together with the gradual production of methyl tartaryl ions, which are much less symmetrical than the methyl tartrate molecule, would have a very pronounced effect on the shape of the concentration-rotation curve. Since, however, the curves are very similar, it must be assumed that the greater part of the alteration of rotation with variation of concentration is due to solvent action, and that the effect of the dissociation of the molecules into ions (as distinct from solvent action) is of much less importance, as will be seen from the following table.

*Molecular Rotation at 20°.*

	Potassium methyl tartrate.	Δ.	Methyl tartrate.	Δ.	Ethyl tartrate.	Δ.
At infinite dilution...	+46.7°		+38.50°		+55.30°	
Homogeneous salt ...	24.8	21.9°	3.63	34.82°	15.78	39.52°

Thus the total change in the rotation of methyl tartrate due to solution in water is 34.8°, whilst the total change in the rotation of potassium methyl tartrate is considerably less, namely, 21.9°. Now since the total change in the rotation of ethyl tartrate due to solution is only slightly greater than the corresponding change in the rotation of methyl tartrate, it may be assumed that if no dissociation were to take place in potassium methyl tartrate with increasing dilution its rotation also would undergo a change of more than 30° due to solvent action alone. The actual change is, however, less, and this must be

ascribed to the influence of dissociation, which thus exercises a depressing effect on the rotation of potassium methyl tartrate, the opposite to what might, at first sight, be expected. An undissociated molecule in dilute solution has a greater rotation than an ion in the same circumstances.

Again, in spite of the fact that the formula of the molecule of potassium methyl tartrate (or the methyl tartaryl ion) appears more asymmetric than that of the methyl tartrate molecule, there is comparatively little difference in the behaviour of the two substances as regards change of concentration.

A close similarity might have been expected between the normal alkali tartrates and the three alkyl esters, but, on the contrary, the two series are markedly dissimilar. As regards the influence of temperature-change, the two metallic salts behave alike; the rotations of the homogeneous substances diminish with rise of temperature, whereas in dilute solution they increase. With rise of temperature, all three homogeneous esters, however, show a rapidly increasing rotation, whilst in dilute solution the rotation as rapidly, or almost as rapidly, diminishes. Thus, although in the homogeneous state all the molecules are of the same type,  $T\begin{smallmatrix} \text{R} \\ \text{R} \end{smallmatrix}$ , the behaviour of the two series is quite

different, whilst in dilute solutions, where the active groups  $T\begin{smallmatrix} \text{R} \\ \text{R} \end{smallmatrix}$  and  $T\begin{smallmatrix} \text{R} \\ \text{R} \end{smallmatrix}$  are, it might be imagined, at least of the same degree of asymmetry, the behaviour is again opposite.

*The Occurrence of Maximum Rotations.*—It has been shown in the foregoing part of this paper that in several cases maximum rotations occur in certain solutions at definite temperatures, and that in one instance a maximum is apparent in a concentration-rotation curve. The latter, which represents the behaviour of potassium tartrate at  $100^\circ$ , is shown in Fig. 3, and may possibly be explained in the following manner.

The rotation of the homogeneous salt at  $100^\circ$  is  $+58.2^\circ$ . The addition of water gradually increases the rotation of the dissolved substance in much the same way that the rotation of the alkyl tartrates is increased by dilution. On account of this analogy, and also because down to a concentration of about  $p=50$  there is not likely to be much dissociation, this increase in rotation must be ascribed almost entirely to solvent action. If no dissociation at all occurred, then probably the rotation would constantly increase with further dilution. At medium concentrations, however, dissociation becomes appreciable, and potassium tartaryl ions,  $TK-$ , are first formed. Since this brings about a diminution of rotation, these must have a smaller rotation

than the dissolved, undissociated molecule. The curve tends to become, and at  $p=30$  does become, horizontal. With further dilution, tartaryl ions form, and, as these have a still lower rotation, their gradual increase in solution is attended with a constant diminution of rotation. The maximum, therefore, occurs at the concentration at which the potassium tartaryl ions preponderate.

A similar explanation will account for the form of the concentration curve at  $20^\circ$ , but at this temperature it should be noticed that the solvent action of water at high concentrations is not so marked as at  $100^\circ$ . The rotation of an undissociated molecule of potassium tartrate in dilute solution at  $20^\circ$  would presumably be almost the same as the molecular rotation of the homogeneous compound. The concentration-rotation curve, therefore, if no dissociation took place, would be nearly a horizontal straight line. Dissociation into potassium tartaryl ions causes the downward tendency of the curve, which becomes more rapid as dilution increases and tartaryl ions are formed.

It would appear, therefore, that in addition to other points already mentioned, the metallic salts of tartaric acid show an opposite behaviour in respect to the solvent action of water, since, as has just been shown, dilution in concentrated solutions of sodium and potassium tartrates causes a greater increase of rotation at  $100^\circ$  than at  $20^\circ$ , whereas dilution of solutions of the alkyl tartrates produces a much more marked effect at  $20^\circ$  than it does at  $100^\circ$ .

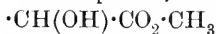
The occurrence of maxima in rotation-temperature curves is rare, the first instance of this having been discovered by P. F. Frankland and Wharton (*Trans.*, 1896, 69, 1587), who showed that ethyl dibenzoyltartrate in the homogeneous condition has a pronounced maximum rotation at  $60^\circ$ . The next examples were discovered by Grossmann and Pötter (*Ber.*, 1904, 37, 84), who found that ammonium and sodium molybdanylmalates in solutions of several concentrations show maximum rotations at  $35^\circ$  and  $50^\circ$  respectively. In the present paper, five other instances at least are described.

In solutions of potassium and sodium tartrates, the maxima are not very pronounced. They can also be readily explained. Since in very dilute solutions of these salts (Figs. 1 and 2) the rotation increases with rise of temperature, at first fairly rapidly, afterwards more slowly, whilst concentrated solutions show an opposite behaviour, the rotation constantly diminishing and rather less rapidly at low temperatures than at higher ones, it seems clear that in solutions of intermediate concentration the influence of the dissociated molecules will preponderate at low temperatures, causing, on the whole, a slight increase of rotation, whilst at higher and increasing temperatures, on the other hand, when the rotation of the dissociated molecules is almost constant, the form of the curve will be chiefly determined by the behaviour of

the undissociated substance present, in consequence of which the rotation diminishes.

The maxima in the rotations of the potassium alkyl tartrates are more interesting and much more pronounced. They are not due to the different behaviour of coexistent but dissimilar active groups, since even the ionic rotations show distinct maxima. Nevertheless, the following explanation—if it is correct—somewhat resembles that given above. From Figs. 8, 9 and 10, it will be seen that, in dilute solution, the rotations of the alkyl tartrates rapidly increase with fall of temperature. On the other hand, the rotations of sodium and potassium tartrates, in dilute solution, increase as the temperature rises.

Now the methyl tartaryl ion, for example, is composed of two parts, one of which,  $\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\cdot\text{CH}_3$ , is the same as either half of the methyl tartrate molecule, whilst the other part,  $\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\cdot$ , is the same as one half of the tartaryl ion. It is therefore possible that in dilute solution each of these parts produces the same effect that it exerts when united to another group like itself. On heating from low temperatures up to about  $30^\circ$ , the influence of the former group is to depress the rotation, whilst that of the latter is to increase it. Thus there are two opposing influences at work, and at first the ionised group exercises the preponderating effect, an increase of rotation being the net result. At a certain temperature, that at which the maximum occurs, these influences become equal. When this temperature has been passed, the group



obtains the ascendancy, and in consequence the rotation diminishes on further heating.

That this supposition is correct seems to be borne out by the following considerations. It will be noticed from Figs. 8, 9, and 10 that the rotation of a methyl tartrate solution ( $p=5.17$ ) between  $0^\circ$  and  $100^\circ$  diminishes by  $6^\circ$ . For ethyl tartrate, the diminution ( $p=4.9989$ ) is  $10.2^\circ$ , whilst for propyl tartrate ( $p=4.02$ ) the rotation falls by  $15.7^\circ$ . We should therefore expect from these figures that the influence of the group  $\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{R}$  would be more marked in potassium propyl tartrate than in potassium ethyl tartrate, and in the latter more than in potassium methyl tartrate. The influence of the group  $\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\cdot$  should therefore, on the other hand, be most apparent in potassium methyl tartrate, so that the initial rise in the curve for this substance should be more rapid and continue further than in the curves for the other two compounds, and the diminution after the maximum is passed should be less. This is in reality what happens. The temperature of maximum rotation is higher for the methyl than for the ethyl compound, and for the latter higher than for potassium propyl tartrate,

whilst the initial rise and subsequent fall in rotation show just the gradation that might be expected.

Now, although maximum rotations are most apparent in the five instances mentioned, it may be noticed that perhaps there is also a maximum in the methyl tartrate solution ( $p=49.77$ ), and it is practically certain that temperature-rotation curves for solutions of concentrations between  $p=50$  and  $p=70$  would exhibit this phenomenon more definitely. As can easily be deduced from the curves in Fig. 4, a solution of  $p=66$ , for instance, would show a maximum at a temperature near  $50^{\circ}$ .

Maximum rotations of this kind can scarcely be explained in either of the two ways mentioned above. The phenomenon must be due solely to solvent action. There is no dissociation to account for it. The form of the curve represents a compromise between the behaviour of the homogeneous ester and its very dilute solutions. The rotation of the pure ester at low temperatures increases on heating, much more rapidly than that of the dilute solution diminishes, whilst at higher temperatures the rotation of the dilute solution diminishes more rapidly than that of the homogeneous ester increases. The net result therefore in a solution of intermediate concentration is a slight initial increase to a somewhat indistinct maximum, with a subsequent slight diminution.

#### *Comparison of Rotation Values.*

The rotations of the alkyl tartrates in the homogeneous condition and in solution are contrasted in the following table:

	$[M]_D^{20^{\circ}}$		$[M]_D^{100^{\circ}}$	
	Homogeneous ester.	Infinitely dilute solution.	Homogeneous ester.	Infinitely dilute solution.
Methyl tartrate.....	+3.63°	+38.5°	+11.00°	+32.2°
Ethyl „ .....	15.78	55.3	27.75	46.8
<i>n</i> -Propyl „ .....	29.66	63.0	40.60	49.6

The total modification of rotation due to solution in each case is most conveniently shown as follows:

#### *Total Change of Molecular Rotation due to Solution.*

	20°.	100°.	$\Delta$ .
Methyl tartrate.....	34.82°	21.20°	13.62
Ethyl „ .....	39.52	19.05	20.30
<i>n</i> -Propyl „ .....	33.34	9.60	24.34

It is apparent from these numbers that the increase of rotation due to solution is by no means a constant function of the original rotation, the values for methyl, ethyl and *n*-propyl tartrates in infinitely dilute solution at  $20^{\circ}$  being respectively 10.46, 3.467, and 2.124 times

as great as the values in the homogeneous condition. On the contrary, the actual increase in rotation at  $20^\circ$ —on the average about  $36^\circ$ —is approximately the same in all three cases, but at  $100^\circ$ , although the alterations in rotation for methyl and ethyl tartrates are again nearly equal, their order of magnitude is reversed, whilst the change for *n*-propyl tartrate is less than half as great as that for either of the other two esters.

The only regularity observable is found in the differences between these numbers, which increase as the series is ascended. That is to say, the change in the rotation of methyl tartrate due to solution is  $13.62^\circ$  less at  $100^\circ$  than at  $20^\circ$ , the figures for ethyl and *n*-propyl tartrates being  $20.30^\circ$  and  $24.34^\circ$  respectively. Temperature-change therefore makes itself most distinctly felt in the case of the *n*-propyl ester and least in that of the methyl ester.

For the potassium alkyl tartrates, we have the following data :

	$[M]_D^{20^\circ}$		$[M]_D^{100^\circ}$	
	Homogeneous substance.	Infinitely dilute solution.	Homogeneous substance.	Infinitely dilute solution.
Potassium methyl tartrate...	+24.8°	+46.7°	+31.1°	+45.8°
„ ethyl „ ...	41.7	60.0	46.8	57.0
„ <i>n</i> -propyl „ ...	51.0	64.7	55.5	60.8

The changes in rotation due to solution are shown below :

*Total Change of Molecular Rotation due to Solution.*

	$20^\circ$ .	$100^\circ$ .	$\Delta$ .
Potassium methyl tartrate .....	$21.9^\circ$	$14.7^\circ$	7.2
„ ethyl „ .....	18.3	10.2	8.1
„ <i>n</i> -propyl „ .....	13.7	5.3	8.4

It will be noticed that the change in rotation due to solution is slightly less for the ethyl than for the methyl compound and least for the *n*-propyl ester. At  $100^\circ$ , the order of magnitude of the changes is the same as at  $20^\circ$ , but the changes are considerably smaller, and by nearly equal amounts, as shown in the column marked  $\Delta$ . Thus the change due to solution for potassium methyl tartrate is  $7.2^\circ$ , for potassium ethyl tartrate,  $8.1^\circ$ , and for potassium propyl tartrate,  $8.4^\circ$  less at  $100^\circ$  than at  $20^\circ$ , numbers which show at least the same gradation as those for the corresponding alkyl tartrates. Indeed, the whole general behaviour of the potassium alkyl tartrates is not unlike that of the alkyl tartrates, another indication that the influence of dissociation is comparatively slight.

It is obvious from the data given above and from the various diagrams that solution in water greatly modifies the rotations of the tartrates under consideration. It was suggested on p. 1117 that the

relationships amongst the data for dilute solutions might show greater regularity than those for the pure compounds, since the former may all be regarded as being determined under the same external conditions. The following tables show to what extent this is the case:

	[M] <sub>D</sub> <sup>20°</sup>			[M] <sub>D</sub> <sup>100°</sup>		
	Homogeneous substance.	Δ.	Infinite dilution.	Homogeneous substance.	Δ.	Infinite dilution.
Methyl tartrate .....	+3.68°	12.27°	+38.5°	+11.0°	16.75°	+32.2°
Ethyl " .....	15.95	13.71	55.3	27.75	46.8	14.6°
n-Propyl " .....	29.66		63.0	40.60	12.85	49.6
Potassium methyl tartrate	+24.8°	16.9°	+46.7°	+31.1°	15.7°	+45.8°
" ethyl "	41.7	9.3	60.0	46.8	8.7	57.0
" n-propyl "	51.0		64.7	55.5		60.8

It will be noticed, as has been previously pointed out (this vol., p. 770), that the increase of rotation in passing from methyl tartrate to the ethyl ester is less at 20°, but greater at 100°, than the increase in passing from ethyl to *n*-propyl tartrate. This is very possibly due to an incorrect choice of temperatures at which to institute comparisons, for it might certainly be expected that the first increment of 2CH<sub>2</sub> should produce a greater effect on rotation than the second. It is, therefore, interesting to observe that both at 20° and 100° in dilute solution the change of rotation in passing from ethyl to *n*-propyl tartrate is less than that in passing from methyl to ethyl tartrate. To a certain degree, therefore, the relationships between the rotations of these esters are simpler when the data for dilute solutions, rather than for the esters themselves, are compared, since the effect of temperature change becomes slightly less anomalous. At the same time, however, the simplification is by no means great. At 20°, the increase of rotation due to the second increment of 2CH<sub>2</sub> is nearly half that due to the first, whilst at 100° it is only one-fifth as great.

The relationships amongst the data for the potassium alkyl esters are comparatively little altered by solution. The second increment of CH<sub>2</sub> in all cases produces a less effect than the first. This change of rotation is less in solution than in the homogeneous condition, and the relationships amongst the data for 20° are much the same as the relationships amongst those for 100°.

Having thus examined the data for the alkyl tartrates and the potassium alkyl tartrates as regards total solvent action, the rotations of all these substances in dilute solution may now be compared with the rotation of the tartaryl ion.

The data for the purpose are tabulated below. The column Δ<sub>1</sub> gives the differences between the rotation of each compound and that of the tartaryl ion; the column Δ<sub>2</sub> contains the differences between the rotations of the mono-alkyl tartaryl ion and those of the alkyl esters.

	$[M]_D^{20}$	$\Delta_1$	$\Delta_2$	$[M]_D^{100}$	$\Delta_1$	$\Delta_2$
Tartaryl ion .....	+61.5°	—	—	+63.25°	—	—
Methyl tartaryl ion .....	46.7	-14.8°	8.2°	45.80	-17.45°	23.60°
Methyl tartrate .....	38.5	-23.0		32.20	-31.05	
Ethyl tartaryl ion .....	60.0	-1.5	4.7	57.00	-6.25	10.20
Ethyl tartrate .....	55.3	-6.2		46.80	-16.45	
<i>n</i> -Propyl tartaryl ion .....	64.7	+3.2	1.7	60.80	-2.45	11.20
<i>n</i> -Propyl tartrate .....	63.0	+1.5		49.60	-13.65	

In these figures, some regularity is apparent. At 20°, the addition of a methyl group to the tartaryl ion brings about a considerable diminution of rotation; a second methyl group produces a further depression, but less than the first. The addition of one ethyl group slightly depresses the rotation of the tartaryl ion, a second effects a greater decrease. The addition of one propyl group increases the rotation above that of the ion, whilst the introduction of a second causes, as in the other two cases, a diminution,\* but the rotation still remains greater than that of the free ion.

At 100°, the changes produced are more pronounced, although of much the same kind, but the rotation is always diminished below that of the tartaryl ion by the addition of one or two alkyl groups.

From what has been said, it must be admitted that the subjection of the substances investigated to conditions as closely similar as possible, namely, solution in water and examination at identical temperatures, is insufficient to reveal any constant connection between chemical composition and rotation. New relationships are found, differing considerably from those obtained with the homogeneous substances, but they are scarcely less complex. It is especially obvious that in every case the influence of temperature changes is of paramount importance in modifying these relationships.

In an earlier paper (this vol., p. 771), a suggestion was made for the comparison of the rotation data of methyl, ethyl, and *n*-propyl tartrates, and based on the temperatures of inactivity of the compounds, these temperatures being regarded as "corresponding."

Now the three potassium alkyl tartrates all show distinct maximum rotations in very dilute solution. The rotation of potassium methyl tartrate, or rather, of the methyl tartaryl ion, reaches a maximum value of +48.1° at a temperature of 46.5°. This is, at least in aqueous

\* This resembles the effect of substituting, successively, the two hydroxylic hydrogen atoms of methyl and ethyl tartrate by acyl groups like  $\text{CH}_3\cdot\text{CO}-$ ,  $\text{C}_6\text{H}_5\cdot\text{CO}-$ ,  $-\text{NO}_2$ , &c. The first substitution is usually accompanied by an increase of molecular rotation, whilst the second brings about a diminution (McCrae and Patterson, Trans., 1900, **77**, 1103; and Frankland, Heathcote, and Miss Hartle, Trans., 1903, **83**, 159).

solution, the greatest rotation which the molecule can possibly have; in the given circumstances, it reaches its configuration of maximum asymmetry. In like manner, the ethyl tartaryl ion has its greatest rotation of  $+60.7^\circ$  at a temperature of  $37^\circ$ , whilst the maximum rotation of the *n*-propyl tartaryl ion, namely,  $+65.1^\circ$ , occurs at a temperature of  $34^\circ$ . Is it possible, then, that temperatures of maximum rotation ought also to be regarded as "corresponding," so that the rotations of the three potassium alkyl esters should be compared either at the temperatures at which the maximum rotations are reached or at temperatures defined in some way by them?

Again, an examination of Figs. 8 and 9 will show that, judging by the general form of the curves, methyl and ethyl tartrates may possibly, in very dilute solution, have maximum rotations at temperatures below  $0^\circ$ , that for ethyl tartrate being the lower, whilst if a maximum occurs in dilute solutions of *n*-propyl tartrate it would be found at a still lower temperature, so that these temperatures would be graded in the same manner for the alkyl tartrates as is actually the case for the potassium alkyl esters, the temperature of maximum rotation being highest in both cases for the methyl and least for the *n*-propyl esters.

Moreover, from Figs. 1 and 2, it seems by no means unlikely that even the ionic rotation for potassium and sodium tartrates would show a maximum above  $100^\circ$ ;<sup>\*</sup> if so, this value ought perhaps to be compared, irrespective of temperature, with the other maxima. The rotation of methyl tartrate in infinitely dilute solution at a temperature below  $0^\circ$  would then be comparable with the rotation of the methyl tartaryl ion at  $46.5^\circ$ , and both with that of the tartaryl ion at a temperature above  $100^\circ$ .

If, in solutions of all the substances examined, maximum rotations actually exist, it is probable that the curves for very dilute solutions in the rotation-temperature diagrams (Figs. 1, 2, 4, 5, 6, 8, 9, and 10) represent, in the case of the alkyl tartrates, only one limb, the descending one; for the potassium alkyl tartrates, both limbs, and for potassium and sodium tartrates again only one limb, the ascending one, of curves which are in all three cases of a similar kind.

<sup>\*</sup> The explanation of the maxima given on p. 1138 would then probably require modification. The maximum ionic rotation could not be accounted for by the different behaviour of dissimilar, but coexistent, groups.

## EXPERIMENTAL DATA.

*Sodium Tartrate.*

The sodium tartrate used was twice recrystallised from water and then corresponded with the formula  $C_4H_4O_6Na_2 \cdot 2H_2O$ .

 I.  $p = 1.77713$  hydrated or  $1.499$  anhydrous salt.

$t$ , †	$\alpha_D^{25}$ (400 mm.).	$d$ .	$[\alpha]_D^{25}$ , *	$[M]_D^{25}$ .
16.7°	+1.890°	1.0096	+26.33°	+60.62°
32.5	1.923	1.0054	26.91	61.94
51.2	1.940	0.9978	27.35	62.96
98.5	1.911	0.9713	27.68	63.71

\* The specific rotations are those of the hydrated salt.

† These and the following observations are recorded in the order in which they were made.

 II.  $p = 4.92493$  hydrated or  $4.154$  anhydrous salt.

$t$ .	$\alpha_D^{25}$ (400 mm.).	$d$ .	$[\alpha]_D^{25}$ .	$[M]_D^{25}$ .
18.5°	+5.277°	1.0282	+26.05°	+59.98°

 III.  $p = 10.1507$  hydrated or  $8.5614$  anhydrous salt.

$t$ .	$\alpha_D^{25}$ (249.6 mm.).	$d$ .	$[\alpha]_D^{25}$ .	$[M]_D^{25}$ .
9.1°	+6.868°	1.0630	+25.50°	+58.69°
23.4	6.977	1.0584	26.01	59.89
37.8	7.038	1.0535	26.36	60.68
98.5	6.820	1.0212	26.35	60.66
62.5	7.000	1.0413	26.53	61.07
13.6	6.918	1.0616	25.72	59.20

 IV.  $p = 29.7125$  hydrated or  $25.06$  anhydrous salt.

$t$ .	$\alpha_D^{25}$ (100 mm.).	$d$ .	$[\alpha]_D^{25}$ .	$[M]_D^{25}$ .
8.6°	+8.698°	1.1936	+24.53°	+56.41°
27	8.757	1.1844	24.89	57.23
45.4	8.752	1.1741	25.09	57.70
98.4	8.400	1.1406	24.79	57.01
81.3	8.540	1.1518	24.96	57.40
70.75	8.615	1.1585	25.03	57.56
51.85	8.750	1.1704	25.16	57.87

 V.  $p = 39.08$  hydrated or  $32.873$  anhydrous salt.

$t$ .	$\alpha_D^{25}$ (40 mm.).	$d$ .	$[\alpha]_D^{25}$ .	$[M]_D^{25}$ .
29.8°	+4.685°	1.2504	+23.97°	+55.18°
9.1	4.692	1.2620	23.79	54.75
98.5	4.429	1.2053	23.51	54.12
68.1	4.595	1.2262	23.98	55.19
50.5	4.651	1.2377	24.04	55.36

VI.  $p = 58.515$  hydrated or  $49.35$  anhydrous salt.

$t.$	$\alpha'_D$ (40 mm.).	$d.$	$[\alpha]_D^C$	$[M]_D^C$
99°	+ 6.405°	1.3586	+ 26.14°	+ 46.32°
89.5	6.482	1.3648	20.29	46.47

*Densities determined.*

I.		II.		III.		IV.		V.		VI.	
$t.$	$d.$	$t.$	$d.$	$t.$	$d.$	$t.$	$d.$	$t.$	$d.$	$t.$	$d.$
17.02°	1.0095	14.91°	1.02921	13.23	1.0617	11.4°	1.1924	12.3°	1.2603	100°	1.3580
25.30	1.0075	27.35	1.02553	27.02	1.0572	26.38	1.1849	35.7	1.2468	—	—
31.25	1.0057	—	—	48.2	1.0481	51.6	1.1706	55.3	1.2347	—	—
45.2	1.0005	—	—	95	1.0203	77.6	1.1542	99.3	1.2049	—	—
46.7	0.9998	—	—	—	—	—	—	—	—	—	—
59.8	0.9935	—	—	—	—	—	—	—	—	—	—

*Potassium Tartrate.*

The potassium tartrate,  $K_2C_4H_4O_6 \cdot \frac{1}{2}H_2O$ , was twice crystallised and dried on porous plate in the air.

I.  $p = 5.64501$  hydrated or  $5.429$  anhydrous salt.

$t.$	$\alpha'_D$ (400 mm.).	$d.$	$[\alpha]_D^C$ *	$[M]_D^C$
16.1°	+ 6.253°	1.0353	+ 26.75°	+ 62.96
29.9	6.320	1.0310	27.07	63.72
99	6.112	0.9937	27.24	64.11
78.7	6.217	1.0074	27.33	64.32
50.35	6.297	1.0227	27.27	64.18

\* The values for specific rotation refer to the hydrated salt.

II.  $p = 10.3707$  hydrated or  $9.974$  anhydrous salt.

$t.$	$\alpha'_D$ (400 mm.).	$d.$	$[\alpha]_D^C$	$[M]_D^C$
12.7°	+ 11.987°	1.0677	+ 27.06°	+ 63.70
21.8	12.017	1.0648	27.21	64.03
71.3	11.948	1.0418	27.65	65.06
98.5	11.732	1.0245	27.60	64.97

III.  $p = 26.6665$  hydrated or  $25.647$  anhydrous salt.

$t.$	$\alpha'_D$ (100 mm.).	$d.$	$[\alpha]_D^C$	$[M]_D^C$
17.4°	+ 8.917°	1.1833	+ 28.26°	+ 66.50
34.2	8.898	1.1753	28.39	66.82
47.4	8.867	1.1681	28.47	66.99
65.5	8.763	1.1578	28.38	66.80
99	8.520	1.1369	28.10	66.14

IV.  $p = 32.12$  hydrated or  $30.89$  anhydrous salt.

$t.$	$\alpha'_D$ (100 mm.).	$d.$	$[\alpha]_D^C$	$[M]_D^C$
18°	+ 11.186°	1.2266	+ 28.39°	+ 66.82°
37.2	11.172	1.2170	28.58	67.23
55.7	11.082	1.2064	28.60	67.31
98	10.624	1.1794	28.04	66.00

V.  $p = 40.645$  hydrated or  $39.09$  anhydrous salt.

$t.$	$\alpha_D^{20}$ (40 mm.).	$d.$	$[\alpha]_D^{20}$	$[M]_D^{20}$
17°	+6.036°	1.2975	+28.62°	+67.35°
29.7	6.021	1.2908	28.69	67.56
68	5.877	1.2683	28.50	67.08
99	5.610	1.2496	27.76	65.32

VI.  $p = 58.777$  hydrated or  $56.53$  anhydrous salt.

$t.$	$\alpha_D^{20}$ (40 mm.).	$d.$	$[\alpha]_D^{20}$	$[M]_D^{20}$
28.2°	+9.993°	1.4607	+29.1°	+68.48°
16.3	10.148	1.4678	29.41	69.20
63.8	9.588	1.4390	28.34	66.70
55.3	9.690	1.4444	28.54	67.16
99	9.090	1.4159	27.31	64.27

VII.  $p = 65.1$  hydrated or  $62.61$  anhydrous salt.

$t.$	$\alpha_D^{20}$ (40 mm.).	$d.$	$[\alpha]_D^{20}$	$[M]_D^{20}$
16.1°	+11.778°	1.5347	+29.47°	+69.36°
36.4	11.507	1.5223	29.03	68.33
99	10.425	1.4829	27.00	63.54

### Densities determined.

I.		II.		III.		IV.		V.		VI.		VII.	
$t.$	$d.$	$t.$	$d.$	$t.$	$d.$	$t.$	$d.$	$t.$	$d.$	$t.$	$d.$	$t.$	$d.$
18.16°	1.03184	12.44°	1.06763	18.97°	1.18262	10°	1.2304	17.7°	1.2970	20.5°	1.4654	27.7°	1.5276
29.89	1.03133	24.65	1.06384	27.8	1.1786	28.66	1.2214	29.93	1.2906	42	1.4525	47.8	1.5153
49.05	1.0235	50.6	1.0528	48.7	1.1680	49	1.2103	48.45	1.2798	79.3	1.4290	81	1.4946
78.5	1.0074	81.4	1.0354	76.8	1.1513	78	1.1926	81	1.2605	—	—	—	—

*Potassium Methyl Tartrate.*—The rotation of solutions of potassium, sodium, lithium, calcium, and barium tartrates have already been determined by Fayollat (*Compt. rend.*, 1893, 117, 630), but only at one concentration and at atmospheric temperature. The preparation of potassium methyl tartrate was originally described by Guérin (*Annalen*, 1837, 22, 250), who obtained a salt containing half a molecule of water of crystallisation.

The specimen employed corresponded with the formula  $C_4H_4O_6(CH_3)K$ , and was obtained in moderately large asymmetric crystals having a very distinct cleavage parallel to the longest axis; it decomposed with frothing at  $216$ — $217^\circ$ , but showed indefinite signs of melting several degrees lower.

I.  $p = 5.3067$ .

$t$ .	$\alpha_D^c$ (400 mm.).	$d$ .	$[\alpha]_D^c$ .	$[M]_D^c$ .
10.6°	+4.869°	1.0272	+22.33°	+45.11°
21.5	4.970	1.0243	22.86	46.17
17.2	4.920	1.0253	22.61	45.66
30	5.032	1.0220	23.19	46.85
41.2	5.071	1.0177	23.48	47.42
52.6	5.045	1.0124	23.47	47.42
65.7	4.987	1.0054	23.37	47.20
99	4.707	0.9834	22.55	45.55
14.7	4.900	1.0259	22.50	45.45

II.  $p = 15.1501$ .

$t$ .	$\alpha_D^c$ (400 mm.).	$d$ .	$[\alpha]_D^c$ .	$[M]_D^c$ .
7.7°	+13.763°	1.0801	+21.02°	+42.47°
20.7	14.235	1.0759	21.83	44.10
15	14.054	1.0779	21.52	43.46
27.8	14.360	1.0732	22.08	44.60
39.9	14.557	1.0680	22.49	45.44
52.9	14.573	1.0613	22.66	45.77
75.7	14.300	1.0479	22.52	45.49
98	13.880	1.0321	22.19	44.83

III.  $p = 24.9555$ .

$t$ .	$\alpha_D^c$ (100 mm.).	$d$ .	$[\alpha]_D^c$ .	$[M]_D^c$ .
10.6°	+5.744°	1.1349	+20.28°	+40.98°
35.6	6.036	1.1237	21.52	43.48
52.2	6.086	1.1145	21.88	44.20
63.2	6.066	1.1078	22.03	44.51
99	5.823	1.0819	21.57	43.57
15.1	5.807	1.1330	20.54	41.49

IV.  $p = 47.085$ .

$t$ .	$\alpha_D^c$ (40 mm.).	$d$ .	$[\alpha]_D^c$ .	$[M]_D^c$ .
10.1°	+4.267°	1.2758	+17.76°	+35.87°
24.3	4.510	1.2672	18.90	33.17
17.7	4.337	1.2712	18.32	37.02
33	4.583	1.2617	19.29	33.96
70.4	4.667	1.2360	20.05	40.50
99	4.583	1.2150	20.03	40.46

*Densities determined.*

I.		II.		III.		IV.	
$t$ .	$d$ .	$t$ .	$d$ .	$t$ .	$d$ .	$t$ .	$d$ .
16.7°	1.0255	16.6°	1.0774	13.6°	1.1336	15.1°	1.2727
30.0	1.0220	26.3	1.0739	26.7	1.1279	31	1.2631
47.6	1.0146	40.2	1.0679	49.3	1.1162	43	1.2519
63.9	1.0062	59.1	1.0580	56.1	1.1120	63.1	1.2411
78	0.9981	64.5	1.0548	82.3	1.0949	79.2	1.2297
—	—	77.5	1.0468	—	—	—	—

*Potassium Ethyl Tartrate*.—This compound, which was also described by Guérin (*Annalen*, 1837, 22, 250), has been partially examined as regards rotation by Fayollat (*Compt. rend.*, 1893, 117, 630).

The specimen employed showed a slight appearance of melting at  $205^{\circ}$  and decomposed suddenly at  $212^{\circ}$ . When heated at  $120^{\circ}$ , it lost no weight, and analysis indicated the formula  $C_4H_4O_6(C_2H_5)K$ .

I.  $p = 5.06845$ .

$t$ .	$\alpha_D^{20}$ (400 mm.).	$d$ .	$[\alpha]_D^{20}$ .	$[M]_D^{20}$ .
$8.1^{\circ}$	$+5.577^{\circ}$	1.0236	$+26.87^{\circ}$	$+58.05^{\circ}$
14.9	5.627	1.0223	27.14	58.63
23.2	5.676	1.0203	27.44	59.27
40.4	5.704	1.0144	27.73	59.90
61.1	5.570	1.0049	27.34	59.05
75.4	5.437	0.9962	26.92	58.14
98	5.194	0.9793	26.16	56.51

II.  $p = 15.1035$ .

$t$ .	$\alpha_D^{20}$ (400 mm.).	$d$ .	$[\alpha]_D^{20}$ .	$[M]_D^{20}$ .
$15^{\circ}$	$+16.930^{\circ}$	1.0700	$+26.19^{\circ}$	$+56.57^{\circ}$
7.6	16.717	1.0723	25.81	55.74
23.6	17.083	1.0670	26.50	57.24
39.4	17.106	1.0603	26.70	57.68
56.3	16.943	1.0512	26.68	57.63
78.3	16.407	1.0329	26.29	56.80
98	15.863	1.0235	25.65	55.41

III.  $p = 34.747$ .

$t$ .	$\alpha_D^{20}$ (100 mm.).	$d$ .	$[\alpha]_D^{20}$ .	$[M]_D^{20}$ .
$7^{\circ}$	$+9.895^{\circ}$	1.1750	$+24.23^{\circ}$	$+52.35^{\circ}$
19.7	10.096	1.1687	24.86	53.70
37	10.190	1.1589	25.31	54.66
54.6	10.140	1.1480	25.42	54.91
74.2	9.910	1.1348	25.13	54.29
99	9.560	1.1170	24.63	53.20

IV.  $p = 46.787$

$t$ .	$\alpha_D^{20}$ (100 mm.).	$d$ .	$[\alpha]_D^{20}$ .	$[M]_D^{20}$ .
$14.6^{\circ}$	$+13.566^{\circ}$	1.2380	$+23.42^{\circ}$	$+50.59^{\circ}$
25.1	13.684	1.2314	23.75	51.30
40.2	13.907	1.2215	24.33	52.56
56.8	13.846	1.2099	24.49	52.90
72.2	13.677	1.1988	24.39	52.67
98.6	13.267	1.1787	24.06	51.97

*Densities determined.*

I.		II.		III.		IV.	
$t$ .	$d$ .	$t$ .	$d$ .	$t$ .	$d$ .	$t$ .	$d$ .
13.3°	1.0226	13.1°	1.0706	13.3°	1.1720	31.7°	1.2271
22.05	1.0206	30.51	1.0643	32.42	1.1616	52.0	1.2130
31.37	1.0177	55.3	1.0518	47.9	1.1524	63.5	1.2050
47.9	1.0114	80	1.0369	64.7	1.1413	79.3	1.1933
79.2	0.9937	—	—	79	1.1314	—	—

*Potassium n-Propyl Tartrate.*

In preparing potassium *n*-propyl tartrate, 94 grams of *n*-propyl tartrate were dissolved in about 200 c.c. of *n*-propyl alcohol and a hot solution of 22.5 grams of pure potassium hydroxide in the same alcohol added slowly, with constant stirring. A turbidity ensued, and on cooling the whole mass became solid. Owing to this tendency of the substance to set with water like a soap, its purification was difficult. A small quantity of water was added and the mixture heated on the water-bath. An amount of acetone, insufficient to bring about precipitation, was then added, and the solution repeatedly passed through a double filter-paper surrounded with a steam-jacket, but this did not give a perfectly clear filtrate. The product, on cooling, became almost solid, and the adhering liquid was removed as completely as possible at the pump, and the solid washed with acetone. The cake thus obtained was triturated with acetone in order to remove the *n*-propyl alcohol completely, filtered at the pump, spread on a porous plate, and allowed to dry in the air, 38 grams of the salt being thus obtained. The melting point was not sharp, the substance softening and showing signs of melting at  $161^{\circ}$ , and decomposing with frothing at  $192^{\circ}$ .

0.8000 yielded 0.3042  $K_2SO_4$ .  $K = 17.05$ .

$C_4H_4O_6(C_3H_7)K$  requires  $K = 16.96$  per cent.

The whole of the product was again dissolved in a small quantity of hot water and hot *n*-propyl alcohol added until turbidity ensued. The solution was filtered when hot, allowed to cool, and the precipitate, freed from liquid as far as possible at the pump, was then triturated in a beaker with acetone, filtered again, and washed with acetone. The precipitate was then dried on a porous plate in air and finally over sulphuric acid under diminished pressure.

0.6817 yielded 0.2573  $K_2SO_4$ .  $K = 16.92$ .

A solution of this substance was made up, but it was so turbid, owing to the presence of filter-paper fibre and light powder from the porous plates used in drying the material, that observations could only be made with great difficulty. The potassium *n*-propyl tartrate was therefore dissolved in a small quantity of hot water and the solution filtered through a double layer of paper surrounded with a steam-jacket, but, as the filtrate was still turbid, some pure animal charcoal was added, after which it was heated on the water-bath for about 15 minutes and then filtered. This gave a clear filtrate, which was evaporated to dryness in a glass basin on the water-bath and

then dried thoroughly over sulphuric acid under diminished pressure. The following observations were made with this substance :

I.  $p = 4.98903$ .

$t$ .	$\alpha_D^{20}$ (400 mm.).	$d$ .	$[\alpha]_D^{20}$ .	$[M]_D^{20}$ .
8.9°	+5.497°	1.0219	+26.96°	+63.08°
24.1	5.534	1.0179	27.25	63.75
50.6	5.476	1.0077	27.23	63.72
36.8	5.551	1.0135	27.44	64.22
71.4	5.330	0.9967	26.80	62.71
98.4	5.052	0.9788	25.87	60.53

II.  $p = 25.01$ .

$t$ .	$\alpha_D^{20}$ (100 mm.).	$d$ .	$[\alpha]_D^{20}$ .	$[M]_D^{20}$ .
12.4°	+7.108°	1.1105	+25.59°	+59.88°
21.9	7.173	1.1060	25.93	60.68
51.9	7.133	1.0896	26.18	61.25
69.9	6.963	1.0779	25.83	60.45

III.  $p = 48.4602$ .

$t$ .	$\alpha_D^{20}$ (100 mm.).	$d$ .	$[\alpha]_D^{20}$ .	$[M]_D^{20}$ .
8.2°	+14.253°	1.2255	+24.00°	+56.16°
23.7	14.523	1.2157	24.65	57.68
38.1	14.527	1.2058	24.86	58.18
70.2	14.530	1.1826	25.04	58.60
99	13.853	1.1610	24.62	57.61
63.1	14.420	1.1878	25.05	58.63
53.2	14.496	1.1950	25.03	58.58
7.8	14.191	1.2258	23.89	55.90

*Densities determined.*

I.		II.		III.	
$t$ .	$d$ .	$t$ .	$d$ .	$t$ .	$d$ .
13.3°	1.01954	13.3°	1.1101	13.4°	1.2224
22.05	1.01856	33.2	1.1003	29.8	1.2116
29.65	1.01623	47.1	1.0923	50.3	1.1967
49.4	1.0082	61.7	1.0836	80.3	1.1751
79.2	0.9919	81.8	1.0697	—	—

*Methyl Tartrate.*—For rotation values of the homogeneous ester, compare this vol., p. 766.

I.  $p = 5.16915$ .

$t$ .	$\alpha_D^{20}$ (400 mm.).	$d$ .	$[\alpha]_D^{20}$ .	$[M]_D^{20}$ .
17.2°	+4.425°	1.0146	+21.10°	+37.57
30.7	4.348	1.0105	20.81	37.06
49.9	4.205	1.0028	20.28	36.12
64.2	4.055	0.9953	19.71	35.10
99	3.597	0.9731	17.88	31.84
17.4	4.400	1.0145	20.97	37.36

II.  $p = 10.2298$ .

$t$ .	$\alpha_D^t$ (400 mm.).	$d$ .	$[\alpha]_D^t$ .	$[M]_D^t$ .
17.2°	+8.631°	1.0302	+20.47°	+36.47°
30.3	8.535	1.0254	20.34	36.23
47.5	8.278	1.0183	19.87	35.39
66.4	7.845	1.0077	19.03	33.89
99	6.907	0.9849	17.14	30.53
17.5	8.610	1.0300	20.43	36.39

III.  $p = 24.8854$ .

$t$ .	$\alpha_D^t$ (249.6 mm.).	$d$ .	$[\alpha]_D^t$ .	$[M]_D^t$ .
18°	+12.542°	1.0776	+18.74°	+33.37°
35.7	12.255	1.0687	18.46	32.88
54.5	11.690	1.0569	17.81	31.71
17.2	12.537	1.0779	18.73	33.33
99	10.260	1.0356	15.95	28.41
17.4	12.496	1.0778	18.67	33.23

IV.  $p = 49.7715$ .

$t$ .	$\alpha_D^t$ (100 mm.).	$d$ .	$[\alpha]_D^t$ .	$[M]_D^t$ .
16.7°	+8.529°	1.1646	+14.71°	+26.21°
38.3	8.340	1.1487	14.59	25.98
17.4	8.517	1.1642	14.70	26.18
62.7	7.940	1.1287	14.13	25.17
99.5	7.276	1.0968	13.33	23.74
17.1	8.470	1.1645	14.61	26.03
27.8	8.410	1.1566	14.61	26.02

V.  $p = 74.8685$ .

$t$ .	$\alpha_D^t$ (100 mm.).	$d$ .	$[\alpha]_D^t$ .	$[M]_D^t$ .
17.4°	+8.839°	1.2533	+9.42°	+16.77°
28.3	9.065	1.2439	9.74	17.34
44.8	9.255	1.2233	10.06	17.92
65.4	9.322	1.2082	10.31	18.35
98.5	9.229	1.1740	10.50	18.70

*Densities determined.*

I.		II.		III.		IV.		V.	
$t$ .	$d$ .	$t$ .	$d$ .	$t$ .	$d$ .	$t$ .	$d$ .	$t$ .	$d$ .
19.55°	1.01386	17.86°	1.03003	17.65°	1.0778	18.5°	1.1633	16.9°	1.2543
26.37	1.01193	26.73	1.02719	31.77	1.0709	32	1.1536	39.8	1.2333
31.83	1.01016	33.13	1.02474	51.6	1.0593	55.5	1.1349	58	1.2156
48	1.0035	47.7	1.0181	73	1.0450	77.7	1.1161	77	1.1967
78.9	0.9863	77.5	1.0007	—	—	—	—	—	—

*Ethyl Tartrate.*—The ester, prepared by the hydrogen chloride saturation method, had an observed rotation of 9.39° at 20° in a 100 mm. tube. Values for the molecular rotation of undiluted ethyl tartrate at a number of different temperatures will be found in a former paper (this vol., p. 767).

I.  $p = 4.99894$ .

$t$ .	$\alpha_D^c$ (400 mm.).	$d$ .	$[\alpha]_D^c$ .	$[M]_D^c$ .
11.1°	+5.380°	1.0118	+26.53°	+54.76°
28.7	5.306	1.0071	26.35	54.28
43.6	5.117	1.0014	25.56	52.64
65	4.784	0.9905	24.15	49.76
98.3	4.280	0.9690	22.09	45.50
10.7	5.377	1.0120	26.57	54.74

II.  $p = 4.99917$ .

$t$ .	$\alpha_D^c$ (400 mm.).	$d$ .	$[\alpha]_D^c$ .	$[M]_D^c$ .
18.3°	+5.382°	1.0100	+26.65°	+54.89°
12.6	5.402	1.0116	26.70	55.00

### III. $p = 10.0756$ .

$t$ .	$\alpha_v^\circ$ (400 mm.).	$d$ .	$[\alpha]_v^\circ$ .	$[M]_v^\circ$ .
10.3°	+10.840°	1.0235	+26.28°	+54.14°
25.8	10.577	1.0199	25.74	53.01
41.4	10.183	1.0131	24.94	51.38
68.9	9.300	0.9983	23.11	47.62
98	8.417	0.9785	21.34	43.97

IV.  $p = 25.0338$ .

$t$ .	$\alpha_D^c$ (100 mm.).	$d$ .	$[\alpha]_D^c$ .	$[M]_D^c$ .
12°	+ 6.380°	1.0605	+ 24.03°	+ 49.50°
23.3	6.210	1.0559	23.49	48.39
98	4.820	1.0052	19.15	39.46
54.1	5.647	1.0380	21.73	44.77

V.  $p = 50.225$ .

$t$ .	$\alpha_D^\circ$ (100 mm.).	$d$ .	$[\alpha]_D^\circ$ .	$[M]_D^\circ$ .
16.4°	+9.880°	1.1179	+17.60°	+36.25°
31.2	9.630	1.1070	17.32	35.68
50.1	9.334	1.0915	17.03	35.07
98	8.660	1.0490	16.44	33.86

VI.  $p = 75.05$ .

$t$ .	$\alpha_D^{\circ}$ (100 mm.).	$d$ .	$[\alpha]_D^{\circ}$ .	$[M]_D^{\circ}$ .
17.1°	+ 10.264°	1.1697	+ 11.69°	+ 24.08°
29.5	10.718	1.1585	12.33	25.40
50.2	11.447	1.1391	13.39	27.58
68.4	11.653	1.1216	13.84	28.52
98	11.970	1.0915	14.61	30.10

*Densities determined.*

[illegible]

*n-Propyl Tartrate*.—For rotation values of the homogeneous ester, compare this vol., p. 767.

I.  $p = 4.01741$ .

$t$ .	$\alpha_D^{25}$ (400 mm.).	$d$ .	$[\alpha]_D^{25}$ .	$[M]_D^{25}$ .
17°	+4.314°	1.0064	+26.67°	+62.47°
30.2	4.163	1.0027	25.84	60.51
21.1	4.250	1.0053	26.31	61.61
41.4	4.025	0.9986	25.07	58.71
66.8	3.680	0.9852	23.24	54.44
98	3.283	0.9653	21.16	49.57

II.  $p = 6.99482$ .

$t$ .	$\alpha_D^{25}$ (249.6 mm.).	$d$ .	$[\alpha]_D^{25}$ .	$[M]_D^{25}$ .
17.6°	+4.637°	1.0118	+26.25°	+61.47°
45.6	4.317	1.0017	24.68	57.81

III.  $p = 7.00601$ .

$t$ .	$\alpha_D^{25}$ (400 mm.).	$d$ .	$[\alpha]_D^{25}$ .	$[M]_D^{25}$ .
17.1°	+7.411°	1.0120	+26.13°	+61.20°
29	7.173	1.0084	25.40	59.48
47	6.766	1.0010	24.12	56.49

IV.  $p = 10.0198$ .

$t$ .	$\alpha_D^{25}$ (400 mm.).	$d$ .	$[\alpha]_D^{25}$ .	$[M]_D^{25}$ .
16.7°	+10.310°	1.0179	+25.27°	+59.19°
18.8	10.193	1.0172	25.00	58.56
17	10.313	1.0177	25.28	59.21

*Densities determined.*

I.		II.		III.		IV.	
$t$ .	$d$ .	$t$ .	$d$ .	$t$ .	$d$ .	$t$ .	$d$ .
19.3°	1.00584	17.97°	1.01182	17.8°	1.01185	16.9°	1.01779
23.97	1.00463	23.3	1.01032	24.35	1.00998	23.3	1.0158
35.9	1.0007	38.24	1.0048	47.1	1.0008	—	—
55.6	0.9917	56.6	0.9957	—	—	—	—
77.3	0.9794	—	—	—	—	—	—

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CXVI.—*The Influence of Solvents on the Rotation of Optically Active Compounds. Part VI. The Relationship between Solution-volume and Rotation of the Alkyl and Potassium Alkyl Tartrates in Aqueous Solution.*

By THOMAS STEWART PATTERSON.

IN several recent papers (Trans., 1901, 79, 167, 477; 1902, 81, 1097, 1134) the variation which the rotation of ethyl tartrate undergoes with change of solvent has been fully discussed, and an attempt has been made to account for this variation by showing that the magnitude of the rotation in a given solvent corresponds, to some considerable extent, with the volume of the active molecule, at great dilution, in that solvent.

Of the compounds examined for the purposes of the foregoing paper, the greatest interest in this connection attaches to the alkyl tartrates because their molecular volumes in the homogeneous state can be directly measured, and therefore the total change in volume due to solution may be estimated with certainty. In the case of the potassium alkyl tartrates, the molecular volumes of which in the superfused condition can only be arrived at by extrapolation from values obtained in solution, this total change cannot be determined so satisfactorily.

Figures for the molecular solution-volume of ethyl tartrate have been given in a former paper, but the accuracy necessary in determining the specific gravity of dilute solutions for the purpose of calculating solution-volumes was not sufficiently recognised in these earlier experiments, so that the values obtained then differ somewhat from those calculated from the new data.

*Molecular Solution-volume of Ethyl Tartrate in Water at 20°.*

$$\text{Molecular volume at } 20^{\circ} = \frac{206}{1.2053} = 170.91 \text{ c.c. } (\delta^* = 0.998252).$$

No.	<i>p</i> .*	<i>d</i> .*	M.S.V.	$[M]_D^{20^{\circ}}$
1.	0	—	160.1 c.c.	+55.3°
2.	2.01705	1.00280	159.9 "	—
3.	2.02798	1.00282	160.0 "	—
4.	4.99894	1.00963	159.8 "	54.6
5.	4.99917	1.00970	159.6 " }	
6.	10.0756	1.02165	159.5 "	53.5
7.	10.2307	1.02200	159.5 "	—

*Molecular Solution-volume of Ethyl Tartrate in Water at 20°*  
(continued).

No.	$p$ .*	$d$ .*	M.S.V.	$[M]_D^{20^\circ}$ .
8.	25.0338	1.05744	160.2 c.c.	48.73
9.	50.225	1.11526	163.3 „	36.10
10.	75.05	1.1670	166.6 „	24.4
11.	100	—	170.9 „	15.8

\* These letters indicate:  $p$ , grams of substance per 100 grams of solution;  $d$ , sp. gr. of solution at 20°;  $\delta$ , sp. gr. of water at 20°. For the formula used in the calculation of M.S.V., see Trans., 1901, 79, 193.

These values of the molecular solution-volume agree closely with those given in Trans., 1901, 79, 214, for concentrations between  $p=10$  and  $p=100$ , but for a solution of  $p=5$  there is a difference of 0.6 c.c., the volume formerly obtained being 159.1 c.c. For a solution of  $p=25$  the volume 158.25 was given in the original paper, and it was therefore concluded that dilution beyond  $p=10$  brought about a continual diminution of molecular solution-volume so that the volume, estimated by extrapolation, at infinite dilution would be 157.7 c.c.

From the new determinations, however, the concordant results of Nos. 4 and 5 in the foregoing table show that the volume of the ethyl tartrate molecule in a 5 per cent. solution is slightly greater than in a 10 per cent. solution. In order to decide this point definitely two additional solutions ( $p=2$  approximately) were prepared with freshly distilled ester, and their specific gravities carefully determined at 20°. The volumes calculated from these experiments (Nos. 2 and 3) agree closely and are greater than the volumes in a solution of  $p=5$ . Finally, in order to be sure that these results were strictly comparable with the others, a solution (No. 7) of  $p=10.23$  was examined, with the result that the volume calculated agreed exactly with the former value for practically the same concentration (No. 6):

It must therefore be concluded that the dilution of ethyl tartrate with water is accompanied by contraction until a concentration of about  $p=10$  is reached, whilst further dilution causes a slight expansion. By extrapolation from the values determined, the molecular solution-volume at infinite dilution is found to be very nearly 160.1 c.c., which is 2.4 c.c. greater than that given in the original paper.

This expansion with increasing dilution in dilute solution is not peculiar to ethyl tartrate; it occurs also in solutions of numerous other substances, such as alcohols, esters, acetone, pyridine, &c., which are quoted by J. Traube (*Annalen*, 1896, 290, 51), and, as will be

shown in the sequel, methyl and *n*-propyl tartrates exhibit the same behaviour.

It need not be concluded, however, that a minimum volume of ethyl tartrate actually occurs in water at  $p = 10$ ; in a solution of that concentration the volume change which is all ascribed, by the method of calculation, to the ester, is almost certainly the sum of two changes, one in the solvent and one in the solute. All the values given in the tables are doubtless influenced by change in the solvent except the molecular volume, and probably also the molecular solution-volume at infinite dilution, and therefore only these two will be considered in this paper. The total change of volume due to solution is the difference between them; in the case of ethyl tartrate this amounts to 10.8 c.c., the alteration in rotation, which accompanies this contraction, being  $39.6^\circ$ .

Molecular solution volumes of methyl tartrates in water at  $20^\circ$ .

$$\text{Molecular volume at } 20^\circ = \frac{178}{1.3352} = 133.3 \text{ c.c. } (\delta = 0.998252).$$

<i>p.</i>	<i>d.</i>	M.S.V.	$[M]_D^{20^\circ}$ .
0	—	125.8 c.c.	+ 38.5°
5.16915	1.01374	125.6 „	37.4
10.2298	1.02943	125.5 „	36.4
24.8854	1.0766	126.24 „	33.3
49.7715	1.1623	127.7 „	26.15
74.8685	1.2515	130.1 „	16.92
100	—	133.3 „	3.68

From the figures in the foregoing table it would appear that methyl tartrate, as regards solution-volume, behaves much like the ethyl ester, a maximum contraction occurring at or near  $p = 10$ . The extrapolated value for the molecular solution-volume at infinite dilution is, very nearly, 125.8 c.c., so that the total change due to solution is 7.5 c.c., and the corresponding change in rotation is  $34.72^\circ$ .

*Molecular solution-volume of n-propyl tartrate in water at  $20^\circ$ .*

$$\text{Molecular volume at } 20^\circ = \frac{234}{1.1375} = 205.7 \text{ c.c. } (\delta = 0.998252).$$

<i>p.</i>	<i>d.</i>	M.S.V.	$[M]_D^{20^\circ}$ .
0	—	191.5 c.c.	+ 63.0°
4.01741	1.00566	191.4 „	62.01
6.99482	1.01130	191.2 „	61.18
7.00601	1.01130	191.2 „	60.79
10.0198	1.0169	191.5 „	58.8
100	—	205.7 „	29.66

In this case also there appears to be a concentration of maximum contraction occurring at  $p=7$ . The extrapolated value for molecular solution-volume at infinite dilution is 191.5 c.c.; the total change in volume due to solution is therefore 14.2 c.c., the corresponding increase in rotation being  $33.33^\circ$ .

A general idea of the relationship between molecular solution-volume and rotation in these three esters will best be obtained on inspection of the following table :

	I. Total volume change.	II. $\Delta$	III. $\frac{\text{vol. change}}{\text{mol. vol.}} \times 100$	IV. $\Delta$	V. Total rotation change	VI. Rotation change per 1 c.c. vol. change per mole- cule.	VII. $\Delta$
Methyl tartrate	7.5 c.c.	3.3 c.c.	5.63 c.c.	0.67 c.c.	$34.82^\circ$	$4.64^\circ$	0.98°
Ethyl     ,,	10.3   ,,	3.4   ,,	6.32   ,,	0.58   ,,	39.50	3.66	1.31
n-Propyl   ,,	14.2   ,,		6.90   ,,		33.34	2.35	

The total alteration in volume (Col. I), may be regarded as being due to the change from the internal pressure acting on the molecules when dissolved in molecules of their own kind to that exerted on them when under the influence of the internal forces of water. Since it is practically certain that the internal forces of the three homogeneous esters are different, these changes of pressure will also be different, the least alteration occurring in the case of methyl tartrate for which the percentage volume change (Col. III) is smallest. At the same time the alteration in rotation due to a contraction of 1 c.c. per molecule (Col. VI) is greatest for methyl tartrate, a result which might reasonably be expected, since a given contraction in a small molecule would presumably cause a greater change of asymmetry than an equal alteration of volume in a larger molecule.

The foregoing discussion is sufficient to show that perplexing rotation changes, which are difficult to explain otherwise, can at least be brought into harmony by assuming a causal connection between solution-volume and rotation, which seems to indicate that the line of investigation suggested is not unpromising.

The relationship between the solution-volumes and rotations of the potassium alkyl tartrates may be dealt with more briefly. The data calculated from the figures of the foregoing paper are given in the following tables :

*Molecular Solution-volumes of the Potassium Alkyl Tartrates at 20°.*  
( $\delta = 0.998252$ ).

Potassium Methyl Tartrate.

<i>p.</i>	<i>d.</i>	M.S.V.	$[M]_D^{20^\circ}$ .
0	—	102.0 c.c.	+ 46.7°
5.3067	1.0249	103.2 „	45.99
15.1501	1.07625	105.6 „	44.00
24.9555	1.13102	107.2 „	42.02
47.085	1.26995	110.4 „	37.54
100	—	118.0 „	24.8

Potassium Ethyl Tartrate. ( $\delta = 0.998252$ ).

<i>p.</i>	<i>d.</i>	M.S.V.	$[M]_D^{20^\circ}$ .
0	—	119.7 c.c.	+ 60
5.06845	1.02117	120.6 „	59.06
15.1035	1.06843	122.3 „	56.95
34.747	1.16862	125.6 „	53.68
46.787	1.2339	128.1 „	51.02
100	—	137 „	41.7

Potassium *n*-Propyl Tartrate. ( $\delta = 0.998252$ ).

<i>p.</i>	<i>d.</i>	M.S.V.	$[M]_D^{20^\circ}$ .
0	—	137.0 c.c.	+ 64.7
4.98903	1.01912	138.2 „	63.63
25.01	1.10686	142.5 „	60.48
48.4602	1.21842	147.0 „	57.3
100	—	156.1 „	51.0

In these three cases there is no sign of a concentration of maximum contraction. The solution volume diminishes steadily as dilution increases. The values obtained lie on similar, and fairly regular, curves, but since the molecular volumes as well as the molecular solution-volumes at infinite dilution have to be obtained by extrapolation, the estimates of total volume changes due to solution are liable to error.

These volume changes, together with the corresponding rotation changes, are shown in the following table:

	Total volume change.	Total rotation change.
Potassium methyl tartrate .....	16.0 c.c.	21.9°
„ ethyl „ .....	17.3 „	18.3
„ <i>n</i> -propyl „ .....	19.1 „	13.70

The figures in the two columns are related in much the same manner as the corresponding values for the alkyl tartrates. A contraction of 1 c.c. in a molecule of potassium methyl tartrate causes a greater change of rotation than in either of the others. It must be remembered, however, that both series of values are complicated by dissociation phenomena, the volume change being increased (Traube, *Ber.*, 1892, 25, 2524) and the rotation change diminished (see foregoing paper, p. 1135), and therefore the analogy ought not to be pushed too far.

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## CXVII.—*The Comparative Nitrifying Power of Soils.*

By SYDNEY FRANCIS ASHBY, B.Sc., Carnegie Research Scholar.

### Part I.—*Preliminary.*

NITRIFICATION in the soil has been shown by Winogradsky (*Ann. Inst. Pasteur*, 1889—1891, 4 and 5; *Centr. Bakt. Par.*, 2 Abt., ii, 1895 and 1896) and Warington (*Trans.*, 1884, 45, 637; 1891, 59, 484) to be the work of two groups of bacteria, which convert ammonia into nitrites and the latter into nitrates respectively.

As our agricultural crops obtain their nitrogen wholly from the soil by root absorption of nitrates (leguminous plants, however, only in part), it is a matter of practical importance to know the power of a soil for converting its ammonia, derived from the decay of crop residues, farm-yard manure, or even soluble ammoniacal fertilisers, into the assimilable form of nitrate.

If some trustworthy method can be found for comparing the activity of nitrification in different soils, its results will deserve to be classed with chemical and mechanical analyses as a means of gauging fertility. The preliminary work described below has been confined to the devising of a method and to its trial on some soils of known history.

Three methods of attacking the problem readily suggest themselves :

1. A fixed weight of fresh or partially dried soil may be shaken up with water and a small volume of the extract employed for plate inoculation. After incubating the plates for a suitable time at constant temperature, the number of colonies of either nitrite or nitrate organisms are counted and corrected for the weight of soil used; gelatinous silica or washed agar saturated with dilute solutions of nutritive salts provide an appropriate solid medium, with an

ammonium salt added for nitrite bacteria and a nitrite for the nitrate organism. Hiltner (*Arbeiten aus der Biol. Abt. am Kaiserl. Gesundheitsamte*, 1903, Bd. III, Heft 5) has used such a method for determining the number of bacteria, other than nitrifying bacteria, in soils. Objections to this method, as applied to nitrifying organisms, are based on the exceedingly slow growth of their colonies and their very small size, so that other bacteria develop more rapidly and make counting impossible or very inaccurate. Another objection is, that the aqueous extract cannot be depended on to give a fair sample of the nitrifying bacteria contained in soil owing probably to the difficulty of separating them from the soil particles which they invest and bind together in a *Zoogloea*.

2. Nitrification may be allowed to proceed, in a large bulk of soil to which nitrifiable material has been added, for a fixed time, and under conditions most favourable for the process. The nitrates are finally washed out and determined. A modification of this method consists in mixing a small quantity of the soil to be examined with a large bulk of a standard sterilised soil to which nitrifiable matter and calcium carbonate have been added and proceeding as above described. (Compare Withers and Fraps, *Amer. Chem. Soc.*, 1901, 23, 318; 1902, 24, 528; Fraps, *Amer. Chem. J.*, 1903, 29, 225). The great difficulty here is the securing in a large bulk of soil of standard conditions as regards texture, aëration, and proportion of water. An additional, if subsidiary, danger arises from the tendency to denitrification.

3. Small quantities of soil may be inoculated into a suitable culture solution and, after a given time at constant temperature, the nitrites and nitrates formed may be determined. This method was apparently first adopted by Wiley (Dept. of Agriculture, U.S.A., *Year Book*, 1895), who has, however, not continued it. Jensen (*Tidsskrift Landbrugets Planteavl*, 1899, 5) used such a solution for comparing nitrification in various Danish soils, and Remy (*Centr. Bakt. Par.*, 8, 657) has recommended the same method, using, however, only nitrite solutions for determining the activity of the nitrate organism. Quite recently, Ehrenberg (*Landw. Jahrbücher*, 1904, 33, Heft 1), following Remy, has examined by means of solutions many different soil organisms, including nitrifying bacteria; he employed the ammoniacal and nitrite solutions of full strength recommended by Omeliansky (*Centr. Bakt. Par.*, 1899, ii, 5, 539) for pure culture purposes, but has not obtained reasonably concordant results owing probably to too heavy inoculation (10 grams of soil in 100 c.c. of solution). This method for determining the nitrifying power of soils appeared to be the most promising provided that it was possible to obtain a fair sample of soil.

*Soil Sampling.*

In overcoming the initial difficulty of obtaining a really representative sample of soil, an attempt was first made to inoculate sterilised solutions in the field with small quantities of fresh soil picked out from the side of a hole with a sterilised spatula and transferred at once to the flasks. The nitrification results showed no satisfactory concordance. No greater success attended an attempt to employ aqueous extracts of soil. Finally, hollow brass cylinders 10 cm. long and  $2\frac{1}{2}$  cm. bore, sharpened at one end and flanged at the other, were employed. These fitted loosely into glass tubes stoppered with an india-rubber disc. Sterilisation was secured by wrapping the glass tubes containing the cylinders in filter paper and leaving them for some days in a water-oven at  $100^{\circ}$ . By this means, nitrifying bacteria at least would be destroyed. To obtain a sample of soil, a hole is dug, the sides carefully broken to obtain an undisturbed surface, and a brass cylinder inserted at a depth of 10 cm. from the surface (which is not pressed level) and forced horizontally into the soil, withdrawn, and at once transferred with its core of soil to a glass tube. The tube is opened in the laboratory, the soil pushed into a glass dish, cut up with a sterile knife, placed over sulphuric acid under a bell jar, which is then partially exhausted. The drying should not last longer than 48 hours; the soil is then broken down to a powder, passed through a 1 mm. sieve, well mixed, and exactly 0.2 gram of it seeded into a sterilised solution and incubated at  $29-30^{\circ}$ . The drying of the soil should not be continued longer than is necessary to admit of breaking down to pass the 1 mm. sieve, otherwise, owing to their sensitiveness to desiccation, the nitrifying bacteria may be destroyed. Where the brass cylinder cannot be forced home, as in the case with soils containing numerous large stones, the sample is picked out from the walls of the holes along a line 10 cm. deep. The latter method has been adopted for sampling the stony Rothamsted soils.

*Culture Solution.*

In order, as far as possible, to show the effect of the combined action of both nitrite and nitrate organisms, a culture solution was required which would not encourage the accumulation of nitrite, but would admit of it being quickly and fairly completely converted into nitrate.

Warington (Trans., 1884, 45, 637, and July, 1891, 59, 484) has proved that a strong solution of an ammonium salt, seeded directly with soil, accumulates nitrite, which passes only very slowly into nitrate, and not until the greater part of the ammonia has been changed into

the nitrous state; on the other hand, a very dilute solution containing ammonia nitrified readily into nitrate with very little accumulation of nitrite at any stage.

The solution adopted at first, therefore, was one used by Wiley (*loc. cit.*) containing:

Potassium dihydrogen phosphate	1.0 gram	Calcium chloride...	trace
Magnesium sulphate .....	0.5 „	Distilled water ...	1 litre
Ammonium sulphate .....	0.2 „		

This was made up of ten times the above strength, sterilised by boiling on three successive days, well shaken, and 10 c.c. portions removed and diluted to 100 c.c. with distilled water in Erlenmeyer flasks of 250 c.c. capacity. The flasks were plugged with cotton wool and sterilised with their contents in an autoclave at 130° for 20 minutes. From the soil samples, prepared as above described, portions of exactly 0.2 gram were weighed out and introduced into the flasks together with 0.1 gram of calcium carbonate (prepared by finely pounding calcite and sterilising at 120° in an air-oven). Two flasks were always inoculated from each soil sample, and control flasks without soil were incubated with and without additions of calcium carbonate. The flasks were kept in an incubator at a temperature of 29—30°. To form a rough estimate of the progress of nitrification, a few drops were withdrawn from some of the cultures at the end of the second and each succeeding week, and tested with diphenylamine in sulphuric acid.

As it was desired not to bring nitrification to a completion in the case of any, even of the most active soils, the incubation ceased when a moderate diphenylamine reaction was shown by the most tardily nitrifying solution.

Nitrites were estimated after removal from the incubator by acidifying with very dilute sulphuric acid and titrating with *N*/100 permanganate solution standardised by purified silver nitrite. The residual ammonia was then determined by distillation with a minimum quantity of sodium hydroxide into *N*/50 acid and the latter titrated with approximately *N*/100 alkali, methyl-orange being used as indicator. Nitrates were determined after neutralising the excess of alkali with oxalic acid, adding a zinc-copper couple and keeping in a warm chamber for some days. The ammonia was then estimated as before.

Later, Ulsch's more expeditious method was employed for nitrates.

### *Soils.*

The four experiments devised for the purpose of testing the method of soil sampling have been carried out with soils taken from plots

on the Rothamsted experimental area. The known history of these plots as regards manuring and crop production renders them suitable for such a purpose.

The samples have been drawn from plots in Agdell Field and Barn Field.

*Agdell Field.*—This area has been in four-course rotation (wheat, roots, barley, clover, or beans on one half of the field, with bare fallow replacing the leguminous crop on the other half) since 1848. Manuring has been confined to the root crop which has received no manure, mixed minerals, and minerals and nitrogenous manure on respective plots.

The following plots have been sampled :

Plot A0 has been continuously unmanured, fallow replaces a leguminous crop, and the roots have been carted off.

Root crop, average of 13 courses..... 23 $\frac{5}{8}$  cwt. per acre.

Wheat crop, 1903, dressed grain..... 19 $\frac{3}{8}$  bushels ,,

Plot A1, continuously unmanured, with leguminous crop, and roots fed off.

Root crop, average of 13 courses..... 13 $\frac{3}{8}$  cwt. per acre.

Wheat crop, 1903, dressed grain..... 18 $\frac{3}{4}$  bushels ,,

Plot A2 receives mixed minerals, otherwise as in A1.

Root crop, average of 13 courses..... 186 $\frac{7}{8}$  cwt. per acre.

Wheat crop, 1903, dressed grain..... 27 $\frac{3}{4}$  bushels ,,

Plot A3 has received mixed minerals and nitrogenous manure, otherwise as in A1 and A2.

Root crop, average of 13 courses..... 304 $\frac{1}{4}$  cwt. per acre.

Wheat crop, 1903, dressed grain..... 27 $\frac{1}{2}$  bushels ,,

*Barn Field.*—Mangels have been grown here for 29 years successively. The plots sampled were :

Plot 1C, which has received 14 tons of farmyard manure and 2000 lb. of rape cake to the acre.

Mangels (roots), average 28 years ... 24.13 tons per acre.

,, ,, 1903 crop ..... 28.08 ,, ,,

Plot 4C, receiving 2000 lb. rape cake and mixed minerals.

Mangels (roots), average 28 years ... 21.39 tons per acre.

,, ,, 1903 crop ..... 22.89 ,, ,,

G, pasture land opposite plot 1C, having been in grass about 30 years.

*Experiment I.*

This was arranged with the view of observing (1) whether samples from different holes in the same plot produce nitrification to the same extent, (2) how samples from differently manured plots differ as to their nitrifying power, (3) if two seedings from the same sample nitrify culture solutions to the same extent. The plots A0 and A3 in Agdell Field were chosen for the purpose of testing these points.

The total nitrogen in the 1st nine inches of dry soil in 1883 was: Plot A0, 0.123 per cent.; Plot A3, 0.142 per cent. No later nitrogen data are available.

To judge from the treatment, crop production, and the proportion of nitrogen, plot A0 is the most exhausted in the field, and plot A3 the most fertile.

Samples were taken out of two holes (*a* and *b*) in each plot during October 1903 before the wheat stubble was ploughed up.

Nitrification was allowed to proceed for 35 days at 29° before determinations were made, the results of which are given in Table I.

TABLE I.

Sample.	Nitrogen as nitrites.	Nitrogen as ammonia.	Nitrogen as nitrites + nitrate.	Nitrogen as nitrate.	Total nitrogen.	Nitrogen nitrified per 100 parts of total nitrogen.
A0 <i>a</i> 1st ...	0.119	2.700	2.090	1.971	4.790	43.5
A0 <i>a</i> 2nd ...	0.084	2.172	2.512	2.428	4.684	53.5
A0 <i>b</i> 1st ...	1.337	2.395	2.465	1.128	4.860	50.7
A0 <i>b</i> 2nd ...	0.091	3.628	1.057	0.966	4.685	22.5
A3 <i>a</i> 1st.....	0.098	0.411	5.038	4.940	5.448	92.5
A3 <i>a</i> 2nd ...	0.098	0.317	5.025	4.927	5.342	94.0
A3 <i>b</i> 1st.....	0.094	0.293	4.766	4.672	5.059	94.0
A3 <i>b</i> 2nd ...	0.077	0.106	4.884	4.807	4.990	98.0
Control in- cubated without in- oculation (Mean of 2).	0.035	5.001	—	—	5.036	—

It is to be observed in the first place that the solution has answered its purpose by not inhibiting nitrate formation, nitrites having accumulated in only one instance, although oxidation to nitrate was active even in this case. Again, there is no evidence of appreciable loss

from denitrification, which indeed could hardly occur in the presence of the trifling amount of organic matter conveyed by 0.2 gram of soil. It is possible that the lower total nitrogen values for the A0 series may indicate a slight loss of ammonia by the reaction of the ammonium sulphate with calcium carbonate.

The question as to whether samples from different holes in the same plot can give concordant results is answered in the affirmative, as A0a and A0b agree reasonably well with each other as regards percentage of nitrogen nitrified, and the same is true for A3a and A3b. The duplicates from the same sample agree closely (shown by the numerals 1 and 2), indicating that the soil had been reduced to a sufficient fineness by passing the 1 mm. sieve.

With regard to the relative nitrifying power of the soils from the plots A0 and A3, it is evident that one has nitrified nearly twice as much as the other, and, as one might have anticipated, the more active soil is from the A3 plot with its larger crop production and higher proportion of nitrogen.

### *Experiment II.*

Samples were taken from plots A1, A2, and A3 in Agdell Field, and from 1C, 4C, and G in Barn Field, with the view of comparing the relative nitrifying power of these soils with their fertility as judged by such data as crop production and manuring.

A sample from one hole in each plot was taken in December, 1903. Nitrification was allowed to proceed for 30 days at 29°. These results are given in Table II (p. 1165).

In this series, nitrites have been found in three cases out of twelve, and, as in the earlier experiment, they have been added to the nitrate in order to calculate the proportion of total nitrogen nitrified. In this series, there appears to have occurred no loss of nitrogen by volatilisation of ammonia during incubation.

The three Agdell soils indicate a respective "nitrifying power" quite consistent with their known history, but the superior activity of the Barn Field rapecake-minerals plot over the dung-rapecake plot was hardly to be expected, unless by assuming an inhibiting effect caused by the organic matter of the dung, a theory which is not, however, confirmed by later work with the same soils. The pasture soil G has showed very feeble "nitrifying power," due probably to the fact that the soil has not been moved for many years, and was consequently lacking in aëration. This would have the double effect of reducing the numbers of nitrifying bacteria and weakening the activity (virulence) of those present. As this soil effervesces briskly on adding a mineral acid, it is evident that there is no lack of calcium carbonate.

TABLE II.

Sample.	Nitrogen as nitrites.	Nitrogen as ammonia.	Nitrogen as nitrites + nitrate.	Nitrogen as nitrate.	Total nitrogen.	Nitrogen nitrified per 100 parts of total nitrogen.
	mgs.	mgs.	mgs.	mgs.	mgs.	mean
A1 1st .....	0.00	5.94	0.69	0.69	6.63	10.4 } 26.5
A1 2nd .....	2.36	3.75	2.78	0.42	6.53	42.6 } 38.0
A2 1st .....	3.06	2.83	3.47	0.41	6.30	55.1 } 92.9
A2 2nd .....	0.35	5.27	1.39	1.04	6.66	20.9 }
A3 1st .....	0.00	0.35	5.97	5.97	6.32	94.5 }
A3 2nd .....	0.00	0.58	6.11	6.11	6.69	91.4 }
1C 1st .....	0.07	3.05	3.47	3.40	6.52	53.3 } 56.9
1C 2nd .....	0.07	2.50	3.82	3.75	6.32	60.5 }
4C 1st .....	2.52	1.39	4.86	2.34	6.25	77.8 } 79.0
4C 2nd .....	0.00	1.30	5.27	5.27	6.57	80.2 }
G 1st .....	0.00	5.83	0.75	0.75	6.58	11.4 } 9.8
G 2nd .....	0.00	6.10	0.55	0.55	6.65	8.3 }
Control .....	—	6.60	—	—	6.60	—

*Experiment III.*

The soil samples used in the experiment just described were preserved and kept in bell jars over water from December 4th, 1903, until January 18th, 1904 (6 weeks), without any attempt to exclude light.

It was thought that by employing a strong culture solution the period of incubation might be shortened, although Warington has shown that nitrification starts somewhat later in a strong ammoniacal solution even at a high temperature. With this end in view, two strong solutions of different composition were prepared, No. 1 being the solution used in the two earlier experiments, but without dilution; No. 2 was the solution recommended by Omeliansky for the isolation of the nitrite organisms from soil.

No. 1.	
Potassium dihydrogen phosphate.....	10 grams
Magnesium sulphate .....	5 "
Ammonium sulphate.....	2 "
Calcium chloride .....	trace
Distilled water .....	1 litre

No. 2.	
Potassium dihydrogen phosphate.....	1.0 gram
Magnesium sulphate .....	0.5 "
Ammonium sulphate .....	2.0 "
Ferrous sulphate .....	0.4 "
Sodium chloride .....	2.0 "
Distilled water .....	1 litre

The soil samples preserved for 6 weeks were used, 0.2 gram being seeded into 50 c.c. portions from each of the above solutions. For neutralising the nitrous acid formed, 0.5 gram of powdered crystalline magnesium carbonate was added to each flask after sterilising the solution. The incubation temperature was 29°, as before.

At the end of 24 days, the diphenylamine test showed that nitrification was in progress in the No. 1 solution series, but gave no reaction for the No. 2 set. Twenty-five c.c. of liquid were withdrawn from the No. 1 solution series and examined. The results are given in the upper part of Table III. At the end of 30 days, the remaining 25 c.c. were examined, with the result shown in the lower part of the table.

TABLE III.

Sample.	Nitrogen as nitrites.	Nitrogen as ammonia.	Total nitrogen.	Nitrogen nitrified per 100 parts of total nitrogen.
1st. 25 c.c.				
	mgs.	mgs.	mgs.	
A1 .....	0.39	1.80	2.18	18
A2 .....	1.47	1.25	2.72	54
A3 .....	0.70	2.22	2.92	24
1C .....	5.95	0.55	6.50	91
4C .....	1.44	1.20	2.64	54
G .....	0.07	3.12	3.19	2.2
2nd. 25 c.c.				
A1 .....	7.95	7.77	15.72	50.5
A2 .....	9.52	6.52	16.04	59
A3 .....	4.83	11.80	16.63	29
1C .....	13.26	0.4	13.66	97
4C .....	11.06	4.51	15.57	71
G .....	0.28	14.16	14.44	2
A1 + A1.....				17.90
A2 + A2.....				18.76
A3 + A3.....				18.85
1C + 1C.....				20.10
4C + 4C.....				18.21
G + G .....				17.57
Control incubated (no $\text{MgCO}_3$ ).....				27.27
" " (+ 0.5 gram $\text{MgCO}_3$ ) .....				17.77
Loss of nitrogen by adding $\text{MgCO}_3$ .....				—
				35 per cent.

It is evident that, in spite of the long preservation of the samples, nitrification has occurred in every case, and, as might have been

expected from the strength of the solution, nitrites alone have been formed during the 24 and 30 days' incubation.

Owing to the circumstance that the earlier 25 c.c. were taken from the clear liquid overlying the sediment, a very small proportion of the total nitrogen was removed. In the case of 1C, the flask must have been inadvertently shaken. The final 25 c.c. contained the bulk of the total nitrogen. Evidently the bulk of the ammonia had been precipitated as ammonium magnesium phosphate.

The sum of the total nitrogen figures is given for comparison with controls. The nitrogen found in the check solution incubated with 0.5 gram of magnesium carbonate agrees fairly closely with the total quantity in the nitrifying solutions, but is much less than that in an incubated solution to which no carbonate had been added. It is clear then that in a strong ammoniacal solution containing an insoluble carbonate considerable loss of ammonia takes place, in this case amounting to about 35 per cent. during 30 days at 29°.

The No. 2 solution showed nitrification after 38 days in only one case (4C), no trace of nitrite being present in the other five flasks. Here again the loss of nitrogen shown by control solutions with and without carbonate was as much as 50 per cent.

As regards the parts per hundred of nitrogen nitrified in the No. 1 solution, the order of the soils is not the same as with the diluted solution; A1 and A2 are as in the Experiment II (see Table II), but A3 is extremely low, whilst 1C has been more active than 4C. The superiority of the 1C soil is what one would expect from a knowledge of its history in respect of manuring and crop production. As before, the pasture soil G shows very feeble nitrifying power.

The low results for A3 and the failure in the No. 2 solution seem to indicate that the nitrifying power of the soils is affected by prolonged keeping, so that determinations should be made on the freshly-prepared material. The serious loss of ammonia from strong solutions and their inhibition of nitrate formation within a reasonable time excludes their use for "nitrifying power" determinations.

#### *Experiment IV.*

Before finally selecting a standard culture solution for future work, it was decided to make a trial of the diluted Omeliansky medium with the same set of soils. For this purpose, fresh samples were taken early in April, 1904, from the plots which, in the meantime, had been ploughed. The solution was prepared of full strength and 25 c.c. intro-

duced into duplicate sets of flasks and made up to 100 c.c., so that the liquid actually used contained per litre :

Potassium dihydrogen phosphate .....	0.25 gram
Magnesium sulphate .....	0.15 „
Ammonium sulphate .....	0.5 „
Ferrous sulphate.....	0.1 „
Sodium chloride . .....	0.5 „

Each flask received 0.2 gram of soil, and at the same time 0.2 gram of precipitated sterilised calcium carbonate; the incubation temperature was 29° as before. One set of flasks was examined after 30 days and the duplicate set after a further 7 days. The results are set out in Table IV.

TABLE IV.

Sample.	Nitrogen as nitrite.	Nitrogen as ammonia.	Nitrogen as nitrites + nitrate.	Nitrogen as nitrate.	Total nitrogen.	Nitrogen nitrified per 100 parts of total nitrogen.
<i>30 days :</i>						
	mgs.	mgs.	mgs.	mgs.	mgs.	
A1 .....	0.00	10.48	2.78	2.78	13.26	20.9
A2 .....	5.28	7.01	7.98	0.97	14.99	53.2
A3 .....	8.44	3.19	10.43	1.99	13.62	76.6
1C .....	3.43	1.46	11.72	8.29	13.18	88.9
4C .....	6.99	3.57	9.90	2.91	13.47	73.5
Check ...	—	13.34	—	—	13.34	—
<i>37 days :</i>						
A1 .....	0.00	9.72	6.10	6.10	15.82	38.5
A2 .....	4.60	6.87	8.19	3.59	15.46	53.0
A3 .....	8.23	2.43	12.91	4.68	15.34	84.1
1C .....	0.20	0.10	16.17	15.97	16.27	99.4
4C .....	7.75	3.19	12.39	4.64	15.48	79.4
Check ...	—	15.72	—	—	15.72	—

There has apparently been no noteworthy loss of nitrogen, and although nitrites are in most cases present, a satisfactory partial conversion to nitrate has occurred. Nitrification in the two sets of flasks has maintained a similar rate, the additional 7 days' incubation being followed by an increase of nitrogen nitrified throughout. The order of the soils is quite what one would have expected from their known history; 1C has shown the highest nitrifying power and A3 ap-

proaches closely to 4C. As this diluted No. 2 solution has yielded the most satisfactory results, it is proposed to use it in future.

A difficulty arises in connection with the endeavour to express the comparative "nitrifying power" of soils in absolute values; for instance, one might state the power as so much nitrogen nitrified per litre per day, and indeed Ehrenberg (*loc. cit.*) does this. I have, however, never found a trace either of nitrite or nitrate in my solutions during the first fortnight of incubation, and rarely before the end of the third week. When the process does start, it seems to progress with considerable activity, so that after a 30 days' incubation it is during about the last 9 days that nitrification actually occurs. This preliminary period of apparent rest may be abnormally extended, as is indicated by a series started in the original diluted No. 1 solution with the last set of soils, no evidence of nitrification being perceptible for 60 days. As to what actually takes place during this period, but little information is conveyed by saying that the organisms are multiplying, for, if so, whence do they derive their organic nutriment? The nitrogen of the ammonia may supply one necessary element, but, on the other hand, the carbon supply has to be accounted for during a period when the energy provided by the oxidation of ammonia to nitrite and nitrate is not yet being employed. It may be that at first carbon is obtained from the traces of organic matter either contained in the culture solution or conveyed to it in atmospheric dust, so that until the supply is exhausted the organisms may assimilate their food as the majority of other bacteria do. If this were the case, however, one would expect them to grow with some luxuriance and form colonies on such media as nutritive gelatin or glucose agar, but they characteristically refuse to do so.

Until some insight has been gained into the conditions determining the duration of this preliminary inactive period, absolute values for "nitrifying power" covering the whole incubation time cannot be an expression of what has actually occurred. In the meantime, the percentage of total nitrogen nitrified during an equal period gives a reasonable comparison of "nitrifying power."

Further experiments are now in progress for the purpose of comparing the "nitrifying power" of soil taken at various depths in the same plot, and others again for comparing monthly differences in nitrification of the same soil taken at a uniform depth.

### *Summary.*

The method employed consists in :

- (a) Taking a large sample at a constant depth.
- (b) Drying and pulverising the sample to secure uniformity.

- (c) Seeding a very small quantity (0.2 gram) of soil into
- (d) a dilute sterilised culture solution of constant depth.
- (e) Incubation at constant temperature until nitrification has made moderate progress in the least active solution.
- (f) Calculation of results as parts per hundred of total nitrogen nitrified.

The method has justified itself by :

- (1) Yielding samples giving reasonably similar "nitrifying power" from different parts of the same field.
- (2) Causing equal seedings from the same sample to have similar "nitrifying power."
- (3) Minimising loss of nitrogen by denitrification and volatilisation of ammonia during incubation.
- (4) Limiting the incubation period to about 30 days.
- (5) Showing a comparative "nitrifying power" in soils tested which agrees with what would be inferred from their known history.

The investigation is being carried out at the Laboratory of the Lawes Agricultural Trust, to whom my best thanks are due for the use of the laboratory and apparatus. I must express my sense of deep obligation to Mr. A. D. Hall, M.A., Director of the Rothamsted Experimental Station, who suggested the investigation and continued to give me valuable advice throughout.

ROTHAMSTED LABORATORY.

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## CXVIII.—*The Action of Organic Bases on Olefinic Ketonic Compounds.*

By SIEGFRIED RUHEMANN and EDWIN ROY WATSON.

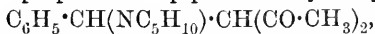
SEVERAL investigators have shown that unsaturated compounds form additive products with organic bases. Goldstein (*Ber.*, 1895, 28, 1450; 1896, 29, 819) obtained such compounds from ethyl benzylidene-malonate, Tambor and Wildi (*Ber.*, 1898, 31, 349) from benzylidene-acetophenone, by combining them with organic bases. One of us, in the course of his researches on the formation of heterocyclic compounds from unsaturated esters, has frequently directed attention to the formation of additive compounds, which preceded the ring formation. In conjunction with Browning (*Trans.*, 1898, 73, 723), he showed that piperidine readily reacts additively with olefinic and acetylenic esters.

We have found lately (Trans., 1904, 85, 466) that aniline forms an additive product with benzylideneacetylacetone, and that the action of other bases on benzylideneacetylacetone and benzylidenebenzoylacetone may also be explained by the assumption that such additive compounds are first formed which subsequently undergo further changes. In continuing the investigation of the behaviour of organic bases towards benzylideneacetylacetone and similar unsaturated ketonic compounds, such as ethyl benzylideneacetoacetate, we have succeeded in isolating several additive compounds. Benzylideneacetylacetone readily yields such additive products with *m*-toluidine, *p*-toluidine, *m*-chloroaniline, *p*-chloroaniline,  $\beta$ -naphthylamine, and piperidine, but benzidine and *p*-phenylenediamine react with the ketone to form dibenzylidenebenzidine and dibenzylidene-*p*-phenylenediamine respectively. Their formation, therefore, is similar to that of benzaldehydephenylhydrazone from benzylideneacetylacetone and phenylhydrazine, and is undoubtedly preceded by the production of unstable additive compounds which at once decompose.

Such additive products of phenylhydrazine and its homologues with ethyl benzylidenemalonate had been obtained by Goldstein (*loc. cit.*), who also found that, on heating, they lose ethyl malonate and yield the phenylhydrazone of benzaldehyde.

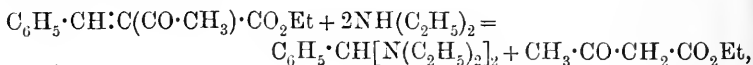
Of especial interest is the fact that neither *o*-toluidine,  $\alpha$ -naphthylamine, nor tetrahydroquinoline reacts with benzylideneacetylacetone. This fact seems to lead to the conclusion that ortho-substituted benzenoid bases do not combine additively with the diketone. A similar observation has been made by Tambor and Wildi (*loc. cit.*), who showed that benzylideneacetophenone does not react with *o*-toluidine, whilst an additive compound is formed with *p*-toluidine. It is remarkable that no such hindrance is manifested in the case of compounds which are so similar to benzylideneacetylacetone as ethyl benzylidenemalonate and ethyl benzylideneacetoacetate. Goldstein (*loc. cit.*) showed that *o*-toluidine and coniine form additive compounds with ethyl benzylidenemalonate, and we find that ethyl benzylideneacetoacetate combines additively with *o*-toluidine just as readily as with aniline.

The study of the properties of piperidobenzylacetylacetone,

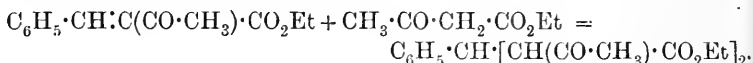


has proved of the greatest interest as throwing light on the catalytic action of piperidine and other secondary bases in the condensations of aldehydes and ketones which have been elaborated by Knoevenagel and his pupils. We have found that this additive compound is stable in a dry atmosphere, but gradually decomposes in the presence of moisture, when the odour of benzaldehyde becomes perceptible. This decomposition is much more marked on heating the substance with

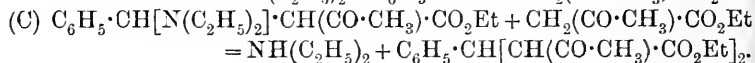
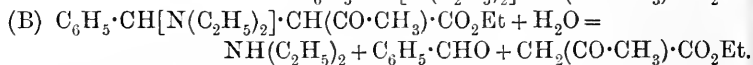
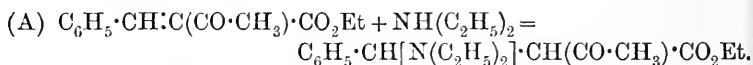
water. The alcoholic solution of this additive compound gradually deposits colourless needles of benzylidenebisacetylacetone, and in this case also the odour of benzaldehyde is developed. This behaviour of the additive compound affords an explanation of Knoevenagel and Faber's observation (*Ber.*, 1898, 31, 2773) that ethyl benzylideneacetoacetate in the presence of diethylamine yields ethyl benzylidenebisacetoacetate. They suggest as an explanation of this reaction that one mol. of ethyl benzylideneacetoacetate under the influence of the amine decomposes thus:



and the ethyl acetoacetate thus formed unites with another molecule of the unsaturated ketonic ester,



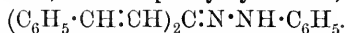
But taking into consideration the foregoing results of our experiments, the following explanation of this reaction must be accepted. First, the base forms with the ethyl benzylideneacetoacetate an additive compound, part of which, in the presence of water, decomposes into benzaldehyde, diethylamine, and ethyl acetoacetate, and the latter then reacts with another molecule of the additive compound to form ethyl benzylidenebisacetoacetate and diethylamine. These changes may be thus expressed:



The correctness of the view that the production of ethyl benzylidenebisacetoacetate is preceded by the formation of the additive compound of the base with ethyl benzylideneacetoacetate is shown also by the following facts: benzylideneacetylacetone, which unites with piperidine, also condenses, as shown by Knoevenagel, with acetylacetone in the presence of the base to form benzylidenebisacetylacetone, whilst we find that no such reaction takes place if tetrahydroquinoline, which does not form an additive compound with the ketone, is used instead of piperidine. The following observation points to the same conclusion: on adding piperidine to ethyl benzylideneacetoacetate, heat is developed, which tends to prove the formation of an additive compound. This substance, however, does not solidify, but remains

viscous if kept in a dry atmosphere; but when exposed to moist air, or on dissolving it in dilute alcohol, crystals separate, and in the course of a day the whole becomes semi-solid. This substance is free from nitrogen and is identical with ethyl benzylidenebisacetoacetate.

We also wish to place on record the results at present arrived at in examining the behaviour of organic bases towards dibenzylideneacetone. We find that this compound differs in its reaction with phenylhydrazine from the olefinic diketones, because it forms with it, not an additive product, but the phenylhydrazone,

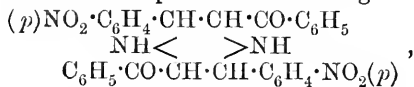


The action of ammonia on dibenzylideneacetone is complicated and yields a mixture of compounds. As yet we have only isolated one substance, which has the formula  $\text{C}_{34}\text{H}_{35}\text{N}_3$ ; its constitution is still unknown.

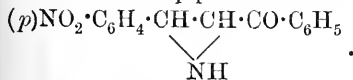
We have also continued the study of the dibromides of benzylideneacetylacetone and benzylideneacetophenone, and have experienced great difficulty in preparing the ethyl ether of benzoylacetylmethane corresponding with the ethyl ether of dibenzoylmethane which we described in our last paper (*Trans.*, 1904, 85, 456). In spite of repeated treatment with alcoholic potash, the product still contains bromine.

In our last paper, we have shown that benzylideneacetophenone dibromide, on treatment with alcoholic potash, yields the ethyl ether of dibenzoylmethane. Recently, Wieland (*Ber.*, 1904, 37, 1150) obtained by the action of alcoholic potash on *p*-nitrobenzylideneacetophenone dibromide, the acetal,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{O} \cdot \text{C}_2\text{H}_5)_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{C}_6\text{H}_5$ . Probably a similar intermediate product is also formed from benzylideneacetophenone dibromide, but this readily loses alcohol—to yield the ethyl ether of dibenzoylmethane.

Wieland further obtained from *p*-nitrobenzylideneacetophenone dibromide and ammonia a compound which he regarded as



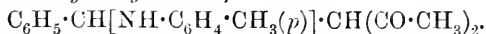
a derivative of piperazine rather than a substance having the formula



By the action of ammonia on benzylideneacetophenone dibromide, we have obtained a compound which, according to the analysis and the molecular weight determination, has the formula  $\text{C}_{15}\text{H}_{13}\text{ON}$ , and therefore is most probably either  $\text{C}_6\text{H}_5 \cdot \text{C}(\text{NH}_2) : \text{CH} \cdot \text{CO} \cdot \text{C}_6\text{H}_5$  or  $\text{C}_6\text{H}_5 \cdot \text{C}(\text{NH}) \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{C}_6\text{H}_5$ . From this fact, it follows that Wieland's substance is monomolecular and is the corresponding amino-nitrobenzylideneacetophenone.

## EXPERIMENTAL.

We have mentioned in the introduction that ortho-substituted benzenoid bases have no action on benzylideneacetylacetone, whilst their isomerides readily form additive products with the diketone. *o*-Toluidine therefore remains unchanged when left with the diketone for weeks, but with *m*- and *p*-toluidines combination takes place in the course of a few hours.

*β-p-Toluidinobenzylacetylacetone,*

—*p*-Toluidine (1 mol.), when mixed with benzylideneacetylacetone (1 mol.), dissolves after a short time; the mixture, when left overnight, sets to a solid which readily dissolves in hot alcohol, and, on cooling, crystallises in colourless needles melting at 96°. The same compound is also formed when the two substances are mixed in alcoholic solution; this product, in the course of a day, sets to a mass of crystals.

0.2109 gave 0.5968 CO<sub>2</sub> and 0.1364 H<sub>2</sub>O. C = 77.13; H = 7.18.

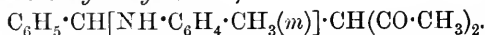
0.1995 „ 8.4 c.c. moist nitrogen at 17° and 758 mm. N = 4.87.

C<sub>19</sub>H<sub>21</sub>O<sub>2</sub>N requires C = 77.28; H = 7.11; N = 4.74 per cent.

On distilling the substance under diminished pressure, acetylacetone first passes over as a colourless oil, and then at 178° under 11 mm. pressure an oil is obtained which sets to a yellow, crystalline mass melting at 29°. This compound is benzylidene-*p*-toluidine, C<sub>6</sub>H<sub>5</sub>·CH:N·C<sub>6</sub>H<sub>4</sub>·CH<sub>3</sub>(*p*). It has been prepared before by Schiff (*Annalen*, 1866, 140, 96) by the action of *p*-toluidine on benzaldehyde; he stated that it melted below 100°. We have compared our product with a specimen which we prepared according to Schiff's directions, and have, moreover, verified its composition by a nitrogen determination.

0.1972 gave 12.2 c.c. moist nitrogen at 15° and 759 mm. N = 7.23.

C<sub>14</sub>H<sub>13</sub>N requires N = 7.18 per cent.

*β-m-Toluidinobenzylacetylacetone,*

—A mixture of equivalent quantities of benzylideneacetylacetone and *m*-toluidine solidifies after 2 hours to a mass of colourless needles, which, when washed with alcohol and dried under diminished pressure, melt at 99–100°.

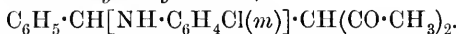
0.2026 gave 0.5747 CO<sub>2</sub> and 0.1303 H<sub>2</sub>O. C = 77.36; H = 7.14.

0.2320 „ 9.6 c.c. moist nitrogen at 15° and 762 mm; N = 4.82.

C<sub>19</sub>H<sub>21</sub>O<sub>2</sub>N requires C = 77.28; H = 7.11; N = 4.74 per cent.

The substance is very soluble in benzene, moderately so in ether, and readily dissolves in hot alcohol.

*β-m-Chloroanilinobenzylacetylacetone,*



—This substance is readily obtained by mixing the ketone and *m*-chloroaniline in alcoholic solution, when the whole slowly sets to a mass of colourless, thin needles, which behave towards solvents similarly to the preceding compound and melt at 93—94°.

0.1998 gave 7.4 c.c. moist nitrogen at 16° and 761.5 mm.  $N = 4.34$ .

$\text{C}_{18}\text{H}_{18}\text{O}_2\text{NCl}$  requires  $N = 4.43$  per cent.

*β-p-Chloroanilinobenzylacetylacetone,*

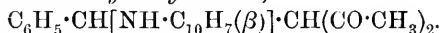


—The alcoholic solution of equivalent quantities of *p*-chloroaniline and benzylideneacetylacetone, when left overnight, sets to a mass of colourless prisms which melt at 99°; these are sparingly soluble in ether, but readily dissolve in hot alcohol.

0.2490 gave 9.5 c.c. moist nitrogen at 17° and 761.5 mm.  $N = 4.43$ .

$\text{C}_9\text{H}_{18}\text{O}_2\text{NCl}$  requires  $N = 4.43$  per cent.

*ββ-Naphthylaminobenzylacetylacetone,*



—An alcoholic solution containing equivalent quantities of *β*-naphthylamine and benzylideneacetylacetone slowly sets to a semi-solid mass of colourless needles, which readily dissolve in hot alcohol and melt at 114°.

0.1673 gave 0.4888  $\text{CO}_2$  and 0.0959  $\text{H}_2\text{O}$ .  $C = 79.68$ ;  $H = 6.36$ .

0.2280 „ 8.6 c.c. moist nitrogen at 18° and 761 mm.  $N = 4.36$ .

$\text{C}_{22}\text{H}_{21}\text{O}_2\text{N}$  requires  $O = 79.75$ ;  $H = 6.34$ ;  $N = 4.23$  per cent.

No additive product is formed from *α*-naphthylamine and benzylideneacetylacetone; the alcoholic solution of the mixture does not deposit any solid even after several weeks.

*Action of Benzidine and of p-Phenylenediamine on Benzylideneacetylacetone.*

Just as the additive product of phenylhydrazine and benzylideneacetylacetone cannot be isolated, but decomposes at once into benzaldehydephenylhydrazone and acetylacetone, so does the corresponding additive compound from benzidine and the ketone decompose into dibenzylidenebenzidine and acetylacetone.

The cold alcoholic solution of the mixture of benzylideneacetylacetone (2 mols.) and benzidine (1 mol.) slowly deposits yellow

crystals; the substance crystallises from benzene in yellow plates melting at 232—233°.

This compound is dibenzylidenebenzidine ( $C_6H_5 \cdot CH:N \cdot C_6H_4$ )<sub>2</sub>.

0.2011 gave 13.4 c.c. moist nitrogen at 14° and 764 mm.  $N = 7.88$ .

$C_{26}H_{20}N_2$  requires  $N = 7.78$  per cent.

The interaction of *p*-phenylenediamine with benzylideneacetylacetone is similar, and in the same circumstances gives rise to dibenzylidene-*p*-phenylenediamine in the form of brown plates melting at 138—140°.

0.1953 gave 0.6048  $CO_2$  and 0.1010  $H_2O$ .  $C = 84.46$ ;  $H = 5.74$ .

0.1998 „ 17.4 c.c. moist nitrogen at 18° and 758.5 mm.  $N = 10.02$ .

$C_{20}H_{16}N_2$  requires  $C = 84.50$ ;  $H = 5.63$ ;  $N = 9.86$  per cent.

#### *Action of Secondary Bases on Benzylideneacetylacetone.*

On gradually adding freshly-distilled piperidine (1 mol.) to benzylideneacetylacetone (1 mol.) cooled by ice, the whole solidifies after a short time; the solid substance, which is  $\beta$ -piperidobenzylacetylacetone,  $C_6H_5 \cdot CH[NC_5H_{10}] \cdot CH(CO \cdot CH_3)_2$ , readily dissolves in hot light petroleum (b. p. 50—70°) and, on cooling, crystallises in beautiful, colourless rhombohedra melting at 93°.

0.1980 gave 0.5418  $CO_2$  and 0.1447  $H_2O$ .  $C = 74.64$ ;  $H = 8.62$ .

0.2335 „ 10.4 c.c. moist nitrogen at 14° and 759 mm.  $N = 5.23$ .

$C_{17}H_{23}O_2N$  requires  $C = 74.72$ ;  $H = 8.42$ ;  $N = 5.13$  per cent.

This compound, although stable when dry, is attacked by water, slowly at the ordinary temperature, but readily on heating, with the formation of benzaldehyde.

If piperidine and benzylideneacetylacetone are mixed in alcoholic solution, colourless needles separate after 24 hours, which are not the above-mentioned additive product, but benzylidenebisacetylacetone. After recrystallisation from alcohol, they melt at 165° (according to Knoevenagel, at 166°).

0.2101 gave 0.5451  $CO_2$  and 0.1329  $H_2O$ .  $C = 70.76$ ;  $H = 7.03$ .

$C_{17}H_{20}O_4$  requires  $C = 70.83$ ;  $H = 6.94$  per cent.

The mother liquor from this reaction contains benzaldehyde and piperidine. It has been stated in the introduction that the formation of benzylidenebisacetylacetone is preceded by the production of the compound  $C_6H_5 \cdot CH[NC_5H_{10}] \cdot CH(CO \cdot CH_3)_2$ , which, in the presence of water, decomposes and yields benzylidenebisacetylacetone. This view is supported by the fact that, in the presence of piperidine, benzylidene-

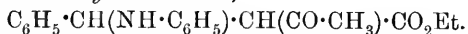
acetylacetone condenses with acetylacetone to form benzylidenebis-acetylacetone, as has already been shown by Knoevenagel, the mixture setting to a solid in the course of a few days.

On using tetrahydroquinoline, however, which does not form an additive compound with benzylideneacetylacetone, the union between this ketone and acetylacetone does not take place even after a few weeks.

Diethylamine, also, reacts additively with benzylideneacetylacetone when the base is gradually added to the diketone cooled in ice. The product is an oil which does not deposit crystals even after a day. If alcohol is added, the oil dissolves, and after a short time the solution sets to a mass of crystals of benzylidenebisacetylacetone.

*Action of Organic Bases on Ethyl Benzylideneacetoacetate.*

*Ethyl  $\beta$ -Anilinobenzylacetoacetate,*



—This compound is readily formed by mixing aniline and freshly-distilled ethyl benzylideneacetoacetate. Heat is developed and, after 3—4 hours, the whole becomes solid. The substance is sparingly soluble in hot light petroleum (b. p. 50—70°) and, on cooling, the solution crystallises in colourless, silky needles which melt at 103°.

0.1719 gave 0.4624  $\text{CO}_2$  and 0.1050  $\text{H}_2\text{O}$  C = 73.36 ; H = 6.78.

0.1994 „ 8.0 c.c. moist nitrogen at 17° and 755 mm. N = 4.62.

$\text{C}_{19}\text{H}_{21}\text{O}_3\text{N}$  requires C = 73.31 ; H = 6.75 ; N = 4.50 per cent.

This compound, on heating under diminished pressure, undergoes a decomposition similar to that which occurs on heating the additive products of aniline and its homologues with benzylideneacetylacetone. In this case, ethyl acetoacetate and benzylideneaniline are formed.

*Ethyl  $\beta$ -o-Toluidinobenzylacetoacetate,*



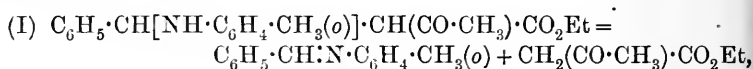
—Whilst from a mixture of benzylideneacetylacetone and o-toluidine there does not separate any solid even after several weeks, ethyl benzylideneacetoacetate readily reacts with the base, and the mixture becomes quite hard in the course of 1—2 days. The solid dissolves in light petroleum (b. p. 50—70°) with great difficulty, but is readily soluble in benzene ; on adding light petroleum to the benzene solution, colourless prisms separate which, after drying under diminished pressure, melt at 89—90°.

0.2030 gave 0.5485  $\text{CO}_2$  and 0.1298  $\text{H}_2\text{O}$ . C = 73.69 ; H = 7.10.

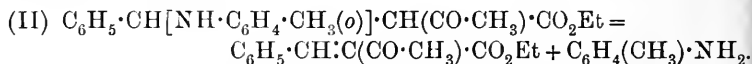
0.2098 „ 7.8 c.c. moist nitrogen at 16° and 761.5 mm. N = 4.34.

$\text{C}_{20}\text{H}_{23}\text{O}_3\text{N}$  requires C = 73.84 ; H = 7.08 ; N = 4.31 per cent.

With the view of ascertaining if this product has a different constitution from the other additive substances obtained by the action of bases on unsaturated ketonic compounds, we have distilled it and have found that it behaves differently from the others in so far as it only partially decomposes to yield benzylidene-*o*-toluidine and ethyl acetoacetate :



whilst another portion yields *o*-toluidine and ethyl benzylideneacetoacetate :



The other additive compounds have been found to decompose entirely in a manner similar to that expressed by the first equation.

On heating under diminished pressure, ethyl *o*-toluidinobenzylacetoacetate, ethyl acetoacetate, and *o*-toluidine first distil over and then at 176—177° under 15 mm. pressure a yellow oil is obtained which was analysed with the following results :

0.2290 gave 0.6635 CO<sub>2</sub> and 0.1350 H<sub>2</sub>O. C = 79.02 ; H = 6.55.

0.2835 „ 10 c.c. moist nitrogen at 17° and 755 mm. N = 4.06.

This oil has been found to be a mixture of almost equivalent quantities of benzylidene-*o*-toluidine and ethyl benzylideneacetoacetate. Their partial separation may be effected by adding light petroleum, which readily dissolves benzylidene-*o*-toluidine, but in which ethyl benzylideneacetoacetate dissolves only slightly. The ketonic ester separates out in colourless crystals melting at 59—60° and having the properties described by Claisen (*Annalen*, 1883, 218, 177). The filtrate, after evaporation of the light petroleum, yields an oil which distils at 179—180°/18 mm. On heating with hydrochloric acid, it decomposes into benzaldehyde and *o*-toluidine, which proves it to be benzylidene-*o*-toluidine.

#### *Action of Piperidine on Ethyl Benzylideneacetoacetate.*

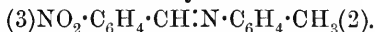
On adding piperidine (1 mol.) to ethyl benzylideneacetoacetate (1 mol.), heat is developed, and a viscous substance is produced which does not set to a solid. This is most probably the additive compound of ethyl benzylideneacetoacetate with the base. When kept in a desiccator over sulphuric acid, no crystals separate even after a week, but the mixture, when exposed to the moist atmosphere, sets to a semi-solid in the course of 2—3 days, and at the same time benzalde-

hyde is eliminated. After washing with dilute alcohol and crystallising the substance from hot alcohol, long, colourless needles are obtained which are free from nitrogen and melt at 152—153°. We have identified this compound with ethyl benzylidenebisacetoacetate by comparison with a specimen prepared according to Knoevenagel's directions.

This transformation of the viscous product takes place much more readily if it is dissolved in dilute alcohol; after a few hours, the solution is filled with the characteristic needles of ethyl benzylidenebisacetoacetate. Ethyl benzylideneacetoacetate therefore resembles benzylideneacetylacetone in its reactions with piperidine.

*Action of o-Toluidine on Ethyl m-Nitrobenzylideneacetoacetate.*

As ethyl benzylideneacetoacetate reacts with *o*-toluidine, so does its *m*-nitro-derivative. In this case, however, we have been unable to isolate the additive compound, because it readily decomposes into ethyl acetoacetate and *m*-nitrobenzylidene-*o*-toluidine,



The reaction takes place if the mixture of the ketonic ester and *o*-toluidine, dissolved in alcohol, is left for 3—4 days. On adding water to the alcoholic solution, a solid is precipitated which crystallises from alcohol in yellow, flat prisms melting at 78—79°.

0.1991 gave 0.5115 CO<sub>2</sub> and 0.0914 H<sub>2</sub>O. C = 70.06; H = 5.10.

0.2005 „ 20.6 c.c. moist nitrogen at 20° and 758 mm. N = 11.71.

C<sub>14</sub>H<sub>12</sub>O<sub>2</sub>N<sub>2</sub> requires C = 70.00; H = 5.00; N = 11.66 per cent.

This substance is readily soluble in alcohol, and with great ease in ether, carbon disulphide, or benzene.

We propose further to examine the part which secondary bases play in the condensation of aldehydes with ketones to form unsaturated ketones. The view that additive compounds are in this case also first produced, seems to follow from the fact that benzaldehyde and acetylacetone condense readily in the presence of piperidine, but not at all in that of tetrahydroquinoline.

*Action of Bases on Dibenzylideneacetone.*

*Phenylhydrazone of Dibenzylideneacetone*, (C<sub>6</sub>H<sub>5</sub>·CH·CH)<sub>2</sub>C·N·NH·C<sub>6</sub>H<sub>5</sub>.

—This compound is formed on adding phenylhydrazine to the boiling alcoholic solution of dibenzylideneacetone. It separates in yellow needles, which melt at 152—153° and dissolve in hot alcohol with difficulty.

0.1723 gave 0.5383  $\text{CO}_2$  and 0.0927  $\text{H}_2\text{O}$ .  $\text{C} = 85.20$  ;  $\text{H} = 5.98$ .

0.2000 „ 15.0 c.c. moist nitrogen at  $20^\circ$  and 769 mm.  $\text{N} = 8.68$ .

$\text{C}_{23}\text{H}_{20}\text{N}_2$  requires  $\text{C} = 85.18$  ;  $\text{H} = 6.17$  ;  $\text{N} = 8.64$  per cent.

*Action of Ammonia on Dibenzylideneacetone.*

An excess of alcoholic ammonia gradually dissolves the ketone, and a white solid separates which increases in quantity in the course of two weeks. This substance dissolves in boiling alcohol with difficulty and, on cooling, crystallises in colourless needles which melt and decompose at  $158^\circ$ .

0.1856 gave 0.5723  $\text{CO}_2$  and 0.1211  $\text{H}_2\text{O}$ .  $\text{C} = 84.09$  ;  $\text{H} = 7.25$ .

0.2065 „ 15.2 c.c. moist nitrogen at  $14^\circ$  and 760 mm.  $\text{N} = 8.66$ .

$\text{C}_{34}\text{H}_{35}\text{N}_3$  requires  $\text{C} = 84.12$  ;  $\text{H} = 7.21$  ;  $\text{N} = 8.63$  per cent.

The larger portion of dibenzylideneacetone is transformed into other substances, which are contained in the yellow filtrate from the compound  $\text{C}_{34}\text{H}_{35}\text{N}_3$ , and are precipitated by water. As yet we have not succeeded in separating the mixture.

*Action of Alcoholic Potash on Benzylideneacetone Dibromide.*

After having proved that benzylideneacetophenone dibromide, on treatment with alcoholic potash, yields the ethyl ether of dibenzoylmethane, we have been desirous of obtaining the corresponding ether of benzoylacetylmethane from benzylideneacetone dibromide. We find, however, that although benzylideneacetone dibromide readily loses 1 mol. of hydrogen bromide under the influence of potassium hydroxide, yet the removal of the second molecule cannot be effected completely. On boiling the dibromide, dissolved in alcohol, with an alcoholic solution containing the exact quantity of potassium hydroxide (2 mols.) on the water-bath for an hour, the solution becomes dark brown, and yields an oil which contains a considerable amount of bromine. If this oil is treated in the same manner with potassium hydroxide, partial decomposition takes place, and a yellow oil is obtained which boils at  $167\text{--}169^\circ$  under 20 mm. pressure and is not yet quite free from bromine. The analytical data, therefore, only agree approximately with the formula  $\text{C}_6\text{H}_5 \cdot \text{C}(\text{O} \cdot \text{C}_2\text{H}_5) : \text{CH} \cdot \text{CO} \cdot \text{CH}_3$  for the ethyl ether of benzoylacetylmethane.

0.2005 gave 0.5486  $\text{CO}_2$  and 0.1357  $\text{H}_2\text{O}$ .  $\text{C} = 74.62$  ;  $\text{H} = 7.44$ .

$\text{C}_{12}\text{H}_{14}\text{O}_2$  requires  $\text{C} = 75.80$  ;  $\text{H} = 7.44$  per cent.

*Aminobenzylideneacetophenone*,  $C_6H_5 \cdot C(NH_2) : CH \cdot CO \cdot C_6H_5$ .

This compound is formed if benzylideneacetophenone dibromide remains in contact with an excess of alcoholic ammonia for two weeks; the solid is collected and dissolved in boiling dilute alcohol, from which, on cooling, it crystallises in almost colourless needles which melt at  $97^\circ$ .

0.1768 gave 0.5229  $CO_2$  and 0.0930  $H_2O$ .  $C = 80.66$ ;  $H = 5.84$ .

0.1882 „ 10.5 c.c. moist nitrogen at  $20^\circ$  and 764 mm.  $N = 6.41$ .

$C_{15}H_{13}ON$  requires  $C = 80.71$ ;  $H = 5.83$ ;  $N = 6.28$  per cent.

The molecular weight determination by the freezing point method gave the following result:

0.1995 in 12.23 benzene gave  $\Delta t = -0.352^\circ$ .  $M. W. = 227$ .

$C_{15}H_{13}ON$  requires  $M. W. = 223$ .

The substance dissolves in cold dilute hydrochloric acid, and on adding alkali to the solution it is precipitated unchanged.

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## CXIX.—*Sulphonphenylchloroamides and Sulphontolyl-chloroamides.*

By FREDERICK DANIEL CHATTAWAY.

SOME years ago, Chattaway and Orton published a series of papers\* in which they established the truth of a theory of substitution which had been put forward previously by Armstrong, and partially proved as far as the first stage by Bender and by Stieglitz and Slossen. According to this theory, substitution by halogens in the nucleus of aromatic amines and amides is not a direct process, but takes place in stages; hydrogen attached to the nitrogen is first replaced, and the substituted nitrogen chlorides or bromides thus produced subsequently undergo intramolecular rearrangement.

The intermediate nitrogen halogen compounds can easily be isolated and preserved unchanged if proper conditions are observed; their transformation is brought about by catalytic agents, and results in

\* Trans., 1899, **75**, 1046; 1900, **77**, 134, 789, 797, 800; 1901, **79**, 274, 461, 469, 817; Ber., 1899, **32**, 3573; 1900, **33**, 3057; 1901, **34**, 160, 1074.

the halogen attached to the nitrogen changing places with hydrogen attached to the ring in positions either para or ortho to the nitrogen. The entrance of halogen into a meta-position with respect to the nitrogen has never been observed in such isomeric changes.

Many facts seem to indicate that these intramolecular rearrangements can only occur when the nitrogen is in a quinquivalent condition, and the catalysts which effect them, for example, hydrogen chloride and chlorine, are known to become attached very easily to tervalent nitrogen. The atoms composing the molecule of an aromatic substituted nitrogen chloride or bromide are apparently able to vibrate or rotate as a stable system in equilibrium, but when, owing to union with the catalyst, the nitrogen atom assumes a quinquivalent condition, that is, is moving as part of a system containing a larger number of atoms, the relations of the system are so altered that during the periodic intramolecular motion a phase occurs when a more stable relationship can be assumed, and this change, which is monomolecular, takes place and is followed by a removal of the catalyst, owing to interaction with another molecule of the nitrogen chloride.

The possibility of isolating these intermediate nitrogen chlorides having been established in a large number of substitutions, it was to be expected that given suitable conditions they might be obtained in all similar cases. In a paper entitled "The Action of Sodium Hypochlorite on the Aromatic Sulphonamides," Raper, Thompson, and Cohen (this vol., p. 373), state that benzenesulphonphenylchloroamide is too unstable to be isolated in a pure state.\*

This compound, however, which, according to Armstrong's theory of substitution, is the intermediate substituted nitrogen chloride to be expected in the chlorination of benzenesulphonanilide, can easily be obtained, as can other analogous compounds, if precautions are taken to avoid the presence of catalytic agents which bring about transformation.

The sulphonchloroamides are formed by the action of hypochlorous acid on the corresponding sulphonanilides, and are comparatively stable substances. They crystallise well and can be kept for a long time without change in dry air. They show all the characteristic reactions of chloroamino-derivatives, for example, they react with alcohol, regenerating the sulphonanilide and producing ethyl hypo-

\* These chemists, who were investigating the position taken up by the entrant halogen, have made the interesting observation that the sulphonic group materially influences the extent to which ortho-substitution takes place, *o*-chlorobenzene-sulphonanilide being in this case the main product, whilst in the transformation of acetylphenylchloroamide (Chattaway and Orton, *Trans.*, 1900, **77**, 797) *o*-chloroacetanilide forms only about 5 per cent. of the whole, 95 per cent. of *p*-chloroacetanilide being formed. Dr. Cohen informs me that no systematic attempt was made to isolate the intermediate products.

chlorite, which breaks up into aldehyde and hydrogen chloride, and they liberate iodine quantitatively from hydriodic acid, a reaction which can be employed in their analysis. When dissolved in glacial acetic acid in the presence of a little hydrogen chloride, they readily undergo the isomeric transformations characteristic of unsubstituted acylphenyl nitrogen chlorides.

The direct chlorination of benzenesulphonanilide dissolved in glacial acetic acid by excess of bleaching powder results in the formation of benzenesulphon-2 : 4-dichlorophenylchloroamide. This shows that chlorination in the sulphonanilides takes an exactly similar course to that followed in the chlorination of other anilides, although, as Raper, Thompson, and Cohen have shown (*loc. cit.*), the sulphonic group materially affects the relative proportion of the isomeric chlorobenzenesulphonanilides produced in the first transformation.

*Benzenesulphonphenylchloroamide*,  $C_6H_5 \cdot SO_2 \cdot NCl \cdot C_6H_5$ .

Benzenesulphonphenylchloroamide and all the similar compounds described in this paper may be easily prepared in the following way.

The corresponding sulphonanilide is dissolved in chloroform and the solution thoroughly shaken with excess of a well-cooled solution of hypochlorous acid; the latter is made by adding an excess of potassium hydrogen carbonate to a  $N/2$  sodium hypochlorite solution cooled to  $0^\circ$  by ice.

After shaking the two solutions together for about thirty minutes, it is best to separate the chloroform solution and, to ensure the complete conversion of the sulphonanilide, to shake it again for a further period of thirty minutes with a fresh quantity of cold hypochlorous acid. The chloroform solution is then separated, thoroughly dried by fused calcium chloride, and the chloroform evaporated off in a current of air.

This is most conveniently done by placing the liquid in a shallow evaporating basin over a water-bath containing hot water, and directing over its surface a rapid current of air. The hot water keeps the chloroform solution from being so much cooled by evaporation that it again becomes damp owing to the condensation of aqueous vapour from the air, while the temperature of the liquid never rises above  $12-13^\circ$ .

The chloroamide under these conditions is obtained as a pale yellow, viscid oil which crystallises on cooling to a mass of colourless crystals. If the product does not at once crystallise, it can easily be made to do so by stirring it with a little light petroleum.

The sulphonchloroamides are all moderately easily soluble in chloro-

form, but only sparingly so in light petroleum; they all crystallise well from a mixture of these solvents, and this medium has been employed in their purification throughout, unless some other solvent is specified. As in some cases transformation is very easily brought about, the purification of a chloroamide may be a matter of difficulty; a procedure generally applicable is as follows: the solid is dissolved in a little warm chloroform and the solution filtered and heated slightly, light petroleum is then at once poured into the warm solution until the liquid shows signs of depositing the chloroamide as an oil. If this actually occurs, a further small quantity of chloroform should be added. On cooling the solution, crystals of the chloroamide slowly separate, and can be similarly recrystallised if necessary. When dealing with easily transformed chloroamides, it is necessary to work very carefully and rapidly, and the product, after shaking the crystals about on warm filter-paper to remove any traces of solvent, should be analysed immediately. The sulphonamides crystallise extremely well in very beautiful, transparent crystals, but these are generally so much twinned that their exact shape can be determined only with difficulty.

Benzenesulphonphenylchloroamide crystallises in colourless, thick, flattened prisms (m. p.  $61^{\circ}$ ).

0.4868 liberated I = 36.2 c.c.  $N/10$  I. Cl as  $NCl$  = 13.18.

$C_{12}H_{10}O_2NClS$  requires Cl as  $NCl$  = 13.24 per cent.

*p-Toluenesulphonphenylchloroamide*,  $CH_3 \cdot C_6H_4 \cdot SO_2 \cdot NCl \cdot C_6H_5$ , crystallises in colourless, transparent, somewhat irregularly grown prisms (m. p.  $91^{\circ}$ ).

0.5345 liberated I = 37.6 c.c.  $N/10$  I. Cl as  $NCl$  = 12.48.

$C_{13}H_{12}O_2NClS$  requires Cl as  $NCl$  = 12.59 per cent.

*Benzenesulphon-p-chlorophenylchloroamide*,  $C_6H_5 \cdot SO_2 \cdot NCl \cdot C_6H_4Cl$ , crystallises in short, pale-yellow, four-sided prisms terminated by pyramids. When seen from the side, the crystals look like six-sided plates (m. p.  $97^{\circ}$ ).

0.6090 liberated I = 40.2 c.c.  $N/10$  I. Cl as  $NCl$  = 11.70.

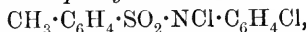
$C_{12}H_9O_2NCl_2S$  requires Cl as  $NCl$  = 11.73 per cent.

*p-Toluene-p-chlorosulphonanilide*,  $CH_3 \cdot C_6H_4 \cdot SO_2 \cdot NH \cdot C_6H_4Cl$ .—This compound and all the sulphonanilides described in the paper were made by warming together for an hour on a water-bath a mixture of equivalent quantities of the aniline and sulphochloride. The product was then again heated on the water-bath with excess of a solution of potassium hydrogen carbonate until the odour of sulphochloride had

practically disappeared. The solid product was collected, powdered, well washed with water, and recrystallised from alcohol.

*p*-Toluene-*p*-chlorosulphonanilide crystallises from alcohol in long, slender, colourless prisms (m. p. 95°).

*p*-Toluenesulphon-*p*-chlorophenylchloroamide,



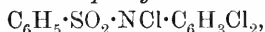
crystallises in very pale yellow plates (m. p. 102°).

0.3445 liberated I = 21.8 c.c. *N*/10 I. Cl as NCl = 11.22.

$\text{C}_{13}\text{H}_{11}\text{O}_2\text{NCl}_2\text{S}$  requires Cl as NCl = 11.21 per cent.

*Benzene-2:4-dichlorosulphonanilide*,  $\text{C}_6\text{H}_5 \cdot \text{SO}_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_3\text{Cl}_2$ , can be prepared either from benzenesulphochloride and 2:4-dichloroaniline or by the interaction with alcohol of the corresponding chloroamide obtained by the direct chlorination of benzenesulphonanilide; it crystallises from alcohol in long, colourless, flattened prisms (m. p. 128°).

*Benzenesulphon-2:4-dichlorophenylchloroamide*,



was prepared in the foregoing manner from benzene-2:4-dichlorosulphonanilide; it crystallises in pale yellow, four-sided plates (m. p. 89°).

0.3438 liberated I = 20.5 c.c. *N*/10 I. Cl as NCl = 10.57.

$\text{C}_{12}\text{H}_8\text{O}_2\text{NCl}_3\text{S}$  requires Cl as NCl = 10.53 per cent.

This compound can also very easily be prepared directly from benzenesulphonanilide, as it is the ultimate product of the chlorination of this substance in the presence of acetic acid.

Benzenesulphonanilide was dissolved in hot glacial acetic acid and a strong solution of bleaching powder was gradually added, when a pale yellow, oily substance separated which solidified on cooling. To ensure complete conversion, this solid was dissolved in hot glacial acetic acid and bleaching powder solution again added, when, as before, the chloroamide separated as an oil which solidified to a crystalline mass on cooling. This was washed with bleaching powder solution and dissolved in a little chloroform. On drying the chloroform solution with fused calcium chloride and adding light petroleum, beautiful, transparent, pale yellow plates of a chloroamide slowly crystallised; these melted at 89° and resembled in every respect the product obtained from 2:4-dichlorosulphonanilide.

0.3560 liberated I = 20.9 c.c. *N*/10 I. Cl as NCl = 10.41 per cent.

On heating with alcohol, it reacted in the way characteristic of chloroamides, yielding ethyl hypochlorite, which rapidly decomposed, forming aldehyde, and 2:4-dichlorosulphonanilide. The latter compound proved to be identical with that obtained from 2:4-dichloroaniline;

they both crystallised in the same form, and melted at the same temperature ( $128^{\circ}$ ), as did also a mixture of the two.

*p-Toluene-2:4-dichlorosulphonanilide*,  $\text{CH}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_3\text{Cl}_2$ .—This compound can be prepared from *p*-toluenesulphochloride and 2:4-dichloroaniline, or, as in the case of the analogous benzenesulphonyl derivative, by direct chlorination of *p*-toluenesulphonanilide; it crystallises from alcohol in brilliant, colourless, transparent, four-sided plates (m. p.  $126^{\circ}$ ).

*p-Toluenesulphon-2:4-dichlorophenylchloroamide*,  
 $\text{CH}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2 \cdot \text{NCl} \cdot \text{C}_6\text{H}_3\text{Cl}_2$ .

—This compound can be prepared either from *p*-toluene-2:4-dichlorosulphonanilide or by the chlorination by bleaching powder solution of *p*-toluenesulphonanilide dissolved in glacial acetic acid; it crystallises in clusters of small, colourless plates (m. p.  $81^{\circ}$ ).

0.5482 liberated  $\text{I} = 31.6$  c.c.  $\text{N}/10$  I. Cl as  $\text{NCl} = 10.22$ .

$\text{C}_{13}\text{H}_{10}\text{O}_2\text{NCl}_3\text{S}$  requires Cl as  $\text{NCl} = 10.11$  per cent.

*Benzenesulphon-p-tolylchloroamide*,  $\text{C}_6\text{H}_5 \cdot \text{SO}_2 \cdot \text{NCl} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_3$ , crystallises in clusters of colourless plates (m. p.  $86^{\circ}$ ).

0.1968 liberated  $\text{I} = 13.7$  c.c.  $\text{N}/10$  I. Cl as  $\text{NCl} = 12.34$ .

$\text{C}_{13}\text{H}_{12}\text{O}_2\text{NClS}$  requires Cl as  $\text{NCl} = 12.59$  per cent.

*p-Toluenesulphon-p-tolylchloroamide*,  $\text{CH}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2 \cdot \text{NCl} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_3$ , crystallises in short, colourless, flattened prisms or plates (m. p.  $109^{\circ}$ ).

0.4052 liberated  $\text{I} = 26.9$  c.c.  $\text{N}/10$  I. Cl as  $\text{NCl} = 11.78$ .

$\text{C}_{14}\text{H}_{14}\text{O}_2\text{NClS}$  requires Cl as  $\text{NCl} = 11.99$  per cent.

*Benzenesulphon-o-tolylchloroamide*,  $\text{C}_6\text{H}_5 \cdot \text{SO}_2 \cdot \text{NCl} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_3$ .—This compound, which, as Raper, Thompson, and Cohen (*loc. cit.*) have shown, can be prepared in acetic acid solution, is, however, more easily obtained by the method previously described; it crystallises in long, colourless, transparent, four-sided prisms with domed ends (m. p.  $106^{\circ}$ ).

0.2577 liberated  $\text{I} = 17.8$  c.c.  $\text{N}/10$  I. Cl as  $\text{NCl} = 12.24$ .

$\text{C}_{13}\text{H}_{12}\text{O}_2\text{NClS}$  requires Cl as  $\text{NCl} = 12.59$  per cent.

*p-Toluenesulphon-o-toluidide*,  $\text{CH}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_3$ , crystallises from alcohol in short, thick, colourless, flattened, six-sided prisms (m. p.  $110^{\circ}$ ).

*p-Toluenesulphon-o-tolylchloroamide*,  $\text{CH}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2 \cdot \text{NCl} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_3$ , crystallises in clusters of colourless, four-sided plates (m. p.  $101^{\circ}$ ).

0.2706 liberated  $\text{I} = 17.9$  c.c.  $\text{N}/10$  I. Cl as  $\text{NCl} = 11.72$ .

$\text{C}_{14}\text{H}_{14}\text{O}_2\text{NClS}$  requires Cl as  $\text{NCl} = 11.99$  per cent.

*m*-Nitrobenzenesulphonanilide,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_5$  crystallises from alcohol, in which it is moderately soluble, in pale yellow plates (m. p.  $126^\circ$ ).

*m*-Nitrobenzenesulphonphenylchloroamide,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2 \cdot \text{NCl} \cdot \text{C}_6\text{H}_5$ , crystallises in small, elongated, six-sided plates or flattened prisms with domed ends, and is pale yellow in colour; it melts at  $106^\circ$  with slight reddening.

0.4880 liberated  $\text{I} = 31.2$  c.c.  $N/10$  I. Cl as  $\text{NCl} = 11.33$ .

$\text{C}_{12}\text{H}_9\text{O}_4\text{N}_2\text{ClS}$  requires Cl as  $\text{NCl} = 11.36$  per cent.

*m*-Nitrobenzenesulphon-*o*-toluidide,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_3$ , crystallises from alcohol, in which it is very sparingly soluble, in very pale yellow, rhombic plates (m. p.  $164^\circ$ ).

*m*-Nitrobenzenesulphon-*o*-tolylchloroamide,  
 $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2 \cdot \text{NCl} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_3$ ,  
 crystallises in very pale yellow, short prisms; it melts at  $118^\circ$  with considerable reddening and decomposition.

0.4144 liberated  $\text{I} = 24.8$  c.c.  $N/10$  I. Cl as  $\text{NCl} = 10.61$ .

$\text{C}_{13}\text{H}_{11}\text{O}_4\text{N}_2\text{ClS}$  requires Cl as  $\text{NCl} = 10.85$  per cent.

*m*-Nitrobenzenesulphon-*p*-toluidide,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_3$ , crystallises from alcohol, in which it is moderately easily soluble, in pale yellow plates (m. p.  $132^\circ$ ).

*m*-Nitrobenzenesulphon-*p*-tolylchloroamide,  
 $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2 \cdot \text{NCl} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_3$ ,  
 crystallises in very pale yellow plates (m. p.  $115^\circ$ ).

0.3800 liberated  $\text{I} = 22.8$  c.c.  $N/10$  I. Cl as  $\text{NCl} = 10.63$ .

$\text{C}_{13}\text{H}_{11}\text{O}_4\text{N}_2\text{ClS}$  requires Cl as  $\text{NCl} = 10.85$  per cent.

*Benzene-m-disulphonanilide*,  $\text{C}_6\text{H}_4(\text{SO}_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_5)_2$ , crystallises from alcohol, in which it is readily soluble, in colourless, transparent, short, six-sided, flattened prisms, which appear to effloresce and become opaque when exposed to the air or on warming. From chloroform, it crystallises in colourless, flattened prisms (m. p.  $150^\circ$ ).

*Benzene-m-disulphonphenylchloroamide*,  $\text{C}_6\text{H}_4(\text{SO}_2 \cdot \text{NCl} \cdot \text{C}_6\text{H}_5)_2$ , crystallises in colourless, transparent, glistening plates; it melts at  $124^\circ$  with slight reddening.

0.3465 liberated  $\text{I} = 30.3$  c.c.  $N/10$  I. Cl as  $\text{NCl} = 15.50$ .

$\text{C}_{18}\text{H}_{14}\text{O}_4\text{N}_2\text{Cl}_2\text{S}_2$  requires Cl as  $\text{NCl} = 15.51$  per cent.

ST. BARTHOLOMEW'S HOSPITAL AND COLLEGE,  
 LONDON, E.C.

CXX.—*Studies in the Camphane Series. Part XV.*  
*Bornylcarbimide.*

By MARTIN ONSLOW FORSTER and HERBERT MOORE ATTWELL.

THE experiments described in this communication arose from an attempt to prepare bornylhydrazine and bornylsemicarbazide, which substances should be optically active, and might be expected therefore to prove themselves serviceable in the resolution of racemic aldehydes and ketones. The only compound of this class at present known in the camphane series is methylbornylhydrazine, which was obtained by reducing nitrosomethylbornylamine with zinc and acetic acid (Forster, *Trans.*, 1899, 75, 943), but the difficulty of preparing it in useful quantities precludes its employment for the purpose mentioned. Bornylcarbamide, on the other hand, is readily obtainable from bornylamine, and we considered it probable that nitrous acid would convert this derivative into a nitroso-compound, which should be reducible to bornylsemicarbazide,  $\text{NH}_2 \cdot \text{N}(\text{C}_{10}\text{H}_{17}) \cdot \text{CO} \cdot \text{NH}_2$ .

On adding sodium nitrite to a salt of bornylcarbamide suspended in water, we were surprised, however, to find that a colourless gas is liberated without producing a nitroso-compound, the solid product consisting of bornylcarbimide, a colourless, crystalline substance which may be distilled in steam. While experiments with this compound were proceeding, our attention was directed to a paper by Doht and Haager (*Monatsh.*, 1903, 24, 844) dealing with the production of phenylcarbimide by the action of nitrous acid on phenylcarbamide, and our preliminary description of bornylcarbimide (*Proc.*, 1904, 20, 91) which followed, led Neville and Pickard to publish an account of the last-named substance, which they prepared by Hofmann's method of distilling the ethyl carbamate with phosphoric oxide (this vol., p. 685).

Being the first optically active isocyanate, we expected that bornylcarbimide would combine the chemical activity of phenylcarbimide with the advantages arising from the presence of a radicle containing an asymmetric carbon atom, and hoped, by its agency, to resolve racemic hydroxy-compounds into their active components. We find, however, that bornylcarbimide is remarkably indifferent to substances containing the hydroxyl radicle, unsuccessful experiments having been made with benzoin, glycerol, the naphthols, and ethyl acetoacetate. Moreover, it is very restricted in its activity towards bases. Substituted carbamides have been obtained by combination with piperidine, aniline, *p*-toluidine, ethylbornylamine, and  $\alpha$ -naphthylamine, whilst phenylhydrazine is converted into symmetrical bornylphenylsemi-

carbazine, but the carbimide does not interact with hydroxylamine, diphenylamine, methylketole, uramil, diazoaminobenzene, carbamide, or acetamide. The fact that the union with  $\alpha$ -naphthylamine is immediate, and attended with considerable development of heat, whereas  $\beta$ -naphthylamine is not affected, adds another to the many points of distinction between these two bases. *ar*-Tetrahydro- $\beta$ -naphthylamine, which has properties similar to those of *p*-toluidine, unlike the latter base, does not unite with bornylcarbimide.

Experiments with the object of producing bornylthiocarbimide have been unsuccessful. As in the case of the ammonium salt, bornylamine thiocyanate is much more stable than the oxygen analogue, and it is not possible to transform it into bornylthiocarbamide by heat, the product consisting of dibornylthiocarbamide. Furthermore, bornyl isocyanide, which we prepared for the same purpose, is so readily hydrolysed to formylbornylamine that the quantity obtained was too small for investigation.

#### EXPERIMENTAL.

*Bornylcarbimide (Bornyl isocyanate)*,  $C_{10}H_{17}\cdot N:C:O$ .

Bornylcarbamide,  $C_{10}H_{17}\cdot NH\cdot CO\cdot NH_2$ , was prepared by heating a solution of bornylamine hydrochloride in water with potassium cyanate, and recrystallising the product from dilute alcohol. A solution containing 0.5386 gram in 25 c.c. of chloroform gave  $\alpha_D$  47' in a 2-dcm. tube, whence  $[\alpha]_D + 18.2^\circ$ .

The *nitrate* of bornylcarbamide was obtained by making a paste of 10 grams of the carbamide with 10 c.c. of concentrated nitric acid, when the product hardened and developed heat; it was filtered, washed, dried in the desiccator, and recrystallised from hot benzene, in which it dissolved readily, separating in minute needles which melt at  $118^\circ$ .

0.1685 gave 23.8 c.c. nitrogen at  $20^\circ$  and 766 mm.  $N = 16.30$

$C_{11}H_{21}O_4N_3$  requires  $N = 16.21$  per cent.

When the nitrate is dissolved in concentrated sulphuric acid, nitric acid is set free, and crushed ice precipitates the *sulphate* of bornylcarbamide, which crystallises from alcohol in lustrous, transparent, six-sided plates melting at  $186^\circ$ . The nitrocarbamide is not produced, and the salt, like the nitrate, is dissociated by boiling water, from which the bornylcarbamide crystallises.

Bornylcarbimide was first prepared from the nitrate of bornylcarbamide in the following manner. Sixty grams of the salt were suspended in water, cooled with crushed ice, and treated with 27 grams of solid sodium nitrite, which was added in small quantities, the

mixture being stirred continuously. Considerable effervescence took place, and nitrous fumes were evolved long after the addition of the nitrite was complete. When 12 hours had elapsed, the product was filtered, washed, and distilled in steam, which removed 8 grams of a colourless, very volatile solid, having an intensely pungent odour, and melting at  $72^{\circ}$ .

The disappointing yield obtained by this process, however, led us to adopt the following modification. Fifty grams of bornylcarbamide were suspended in ice-water and treated with 80 c.c. of concentrated hydrochloric acid; 35 grams of solid sodium nitrite were then added in small quantities during a period of 2—3 hours. Vigorous effervescence attended the addition of the salt, and the gas which was liberated at first was free from nitrous fumes. The suspended solid was ultimately filtered, washed until the filtrate was neutral, and then distilled in steam, which carried over 40 grams of the *isocyanate*, corresponding with a yield of 88 per cent.

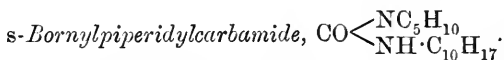
0.2779 gave 19.5 c.c. nitrogen at  $21^{\circ}$  and 767 mm.  $N = 8.06$ .

$C_{11}H_{17}ON$  requires  $N = 7.82$  per cent.

A solution containing 0.9400 gram in 25 c.c. of benzene gave  $\alpha_D 3^{\circ}30'$ , whence  $[\alpha]_D + 46.5^{\circ}$ .

Bornylcarbimide is exceedingly stable for a compound of this class, being unchanged by cold water, although protracted treatment with boiling water transforms it into dibornylcarbamide. It is insoluble in cold dilute acids and alkalis, but in contact with aqueous potassium hydroxide it changes completely into bornylamine in the course of 1 hour. When dropped into concentrated sulphuric acid, the liquid becomes warm, vigorous effervescence occurs, and a clear, colourless solution of bornylamine sulphate is produced.

The substance dissolves readily in organic media, and may be crystallised from alcohol if the hot concentrated solution is rapidly cooled, but if the separation is delayed, the crystals consist of dibornylcarbamide.



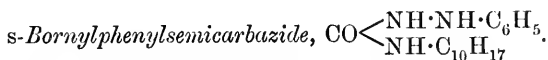
Piperidine (1 mol.) diluted with benzene was added to a solution of bornylcarbimide; heat was developed, and crystals were deposited immediately. After 1 hour, the product was drained and recrystallised from alcohol, from which needles separated melting at  $153^{\circ}$ .

0.2384 gave 22.8 c.c. nitrogen at  $21^{\circ}$  and 759 mm.  $N = 10.88$ .

$C_{16}H_{28}ON_2$  requires  $N = 10.64$  per cent.

A solution containing 0.3387 gram in 50 c.c. of absolute alcohol gave  $\alpha_D 0^{\circ}32.5'$  in a 2-dcm. tube, whence  $[\alpha]_D + 40.0^{\circ}$ . The substance

dissolves very readily in cold organic media, but is only sparingly soluble in boiling water; it is not attacked by hot concentrated aqueous potassium hydroxide.

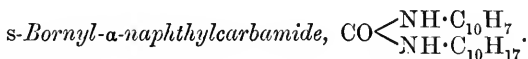


Phenylhydrazine (1 mol.) dissolved in benzene was added to a solution of bornylcarbimide in the same medium, when the liquid became hot, and lustrous, white needles separated; after an hour, the solid was filtered, recrystallised from a mixture of benzene and petroleum, and finally from benzene alone, which deposited minute, silky needles, evolving gas at the melting point,  $140^\circ$ .

0.1658 gave 22.4 c.c. nitrogen at  $28.5^\circ$  and 760 mm.  $N = 14.81$ .

$\text{C}_{17}\text{H}_{25}\text{ON}_3$  requires  $N = 14.63$  per cent.

The semicarbazide dissolves very readily in cold organic media, but it is only sparingly soluble in boiling water. Fehling's solution is reduced very slowly on heating, but cold ammoniacal silver nitrate oxidises an alcoholic solution of the compound immediately.



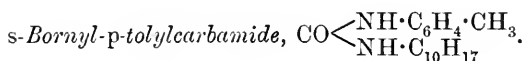
Bornylcarbimide combined very readily with  $\alpha$ -naphthylamine in benzene, the liquid becoming hot and quickly changing to a hard cake of crystals. The product was extracted with hot absolute alcohol, in which it is sparingly soluble, slender, white needles separating as the solution cooled.

0.2024 gave 16.9 c.c. nitrogen at  $26^\circ$  and 767 mm.  $N = 8.94$ .

$\text{C}_{21}\text{H}_{26}\text{ON}_2$  requires  $N = 8.69$  per cent.

The behaviour of the carbamide on heating recalls that of dibornylcarbamide; it remains unmelted in sulphuric acid, but when heated in a dry tube, it melts and sublimes in minute, white needles. In solubility, it lies between dibornylcarbamide and the other derivatives mentioned in this paper; it is very sparingly soluble in boiling petroleum, but dissolves with increasing readiness in benzene, chloroform, and absolute alcohol in the order mentioned.

Neither  $\beta$ -naphthylamine nor *ar*-tetrahydro- $\beta$ -naphthylamine, for a specimen of which we are indebted to Dr. Clarence Smith, appears to combine with bornylcarbimide under the conditions employed in the case of the foregoing compound.

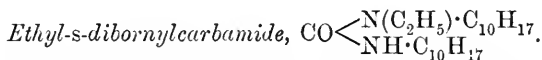


The unexpected contrast between  $\alpha$ - and  $\beta$ -naphthylamines in respect of their behaviour towards bornylcarbimide led us to ascertain whether *p*-toluidine differs from aniline in the same way, and on mixing solutions in benzene it was found that heat is developed and crystals deposited. So readily does combination take place that the two solids fuse when brought together. Crystallisation from alcohol yields the carbamide in large, transparent, six-sided plates melting at 198°.

0.2091 gave 18.6 c.c. nitrogen at 26° and 765 mm.  $N = 9.94$ .

$\text{C}_{18}\text{H}_{26}\text{ON}_2$  requires  $N = 9.78$  per cent.

It is scarcely soluble in boiling petroleum, but dissolves readily in benzene, chloroform, and absolute alcohol.

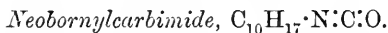


This compound was prepared from ethylbornylamine and bornylcarbimide, which combine very readily in benzene; the effect produced on the fusibility of *s*-dibornylcarbamide by the introduction of the ethyl group is very great, the substituted compound melting at 178°. The same effect is noticed in the case of diphenylcarbamide (m. p. 235°), its ethyl derivative melting at 91°.

0.2749 gave 20 c.c. nitrogen at 24.5° and 767 mm.  $N = 8.22$ .

$\text{C}_{23}\text{H}_{40}\text{ON}_2$  requires  $N = 7.75$  per cent.

The ethyl derivative dissolves much more readily than dibornylcarbamide itself, being freely soluble in benzene and alcohol, whilst boiling petroleum also dissolves it to a moderate extent. A 3 per cent. solution in absolute alcohol is optically inactive.



Neville and Pickard (*loc. cit.*) refer briefly to a crystalline solid having  $[\alpha]_D - 13.4^\circ$ , which was deposited from an oil they obtained by distilling ethyl neobornylcarbamate with phosphoric oxide; the melting point is not given, and it is not stated whether the source of their neobornylcarbamate is the base furnished by fractional crystallisation of the hydrochloride, or the product obtained by hydrolysing the insoluble compound from neobornylamine and ethyl oxalate (Forster and Hart-Smith, *Trans.*, 1900, 76, 1157).

In our experiments, the latter material was used, and proceeding on the lines already described for bornyl carbimide, we have obtained neobornyl carbimide as a volatile, crystalline substance, exactly resembling its isomeride, and melting at  $88^{\circ}$ ; 0.4321 gram dissolved in 25 c.c. of benzene gave  $\alpha_D -1^{\circ}38'$  in a 2-dcm. tube, whence  $[\alpha]_D -47.2^{\circ}$ .

*Conversion of Bornylamine into Camphor.*

The failure to transform bornyl carbamide into a nitroso-derivative and a nitro-compound led us to attempt the production of such derivatives from bornylurethane. On treating this substance with nitrous acid, no change occurred, but cold fuming nitric acid (2 parts) converts it into camphor.

*Bornyl isocyanide,  $C_{10}H_{17} \cdot N : C$ .*

Thirty grams of bornylamine were dissolved in 45 grams of chloroform and treated with 50 grams of potassium hydroxide in 200 c.c. of absolute alcohol, it being necessary to cool the liquid in order to check the violence of the action. After being heated for a short time in a reflux apparatus, the alcohol and chloroform were distilled off, and a current of steam passed through the residue. A small quantity of a solid substance was deposited in the condenser, and after crystallisation from dilute alcohol, melted at  $137^{\circ}$ .

0.1491 gave 0.4383  $CO_2$  and 0.1393  $H_2O$ .  $C = 80.17$ ;  $H = 10.38$ .

0.1757 „ 13.6 c.c. of nitrogen at  $17^{\circ}$  and 745 mm.  $N = 8.80$ .

$C_{11}H_{17}N$  requires  $C = 80.98$ ;  $H = 10.43$ ;  $N = 8.59$  per cent.

The substance is doubtless bornyl isocyanide, and has an odour suggesting both camphor and prussic acid. Owing to the readiness with which it is hydrolysed, however, the yield is very small, the aqueous residue in the distilling flask depositing colourless, lustrous leaflets of formylbornylamine.

0.1512 gave 11.1 c.c. nitrogen at  $19^{\circ}$  and 747 mm.  $N = 8.29$ .

$C_{11}H_{19}ON$  requires  $N = 7.73$  per cent.

This substance was identified by its melting point and specific rotatory power.

*Dibornylthiocarbamide,  $SC \begin{smallmatrix} \text{NH} \cdot C_{10}H_{17} \\ \text{NH} \cdot C_{10}H_{17} \end{smallmatrix}$ .*

Forty-five grams of bornylamine were dissolved in absolute alcohol and heated with 11 grams of carbon disulphide in a reflux apparatus

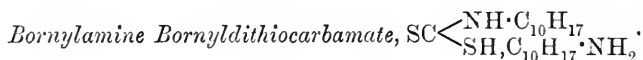
until hydrogen sulphide was no longer evolved, 28 hours' continued heating being required to complete the action. The liquid deposited 9 grams of colourless crystals, which separated from alcohol in slender, hexagonal plates melting at  $227^{\circ}$ .

0.2656 gave 19.9 c.c. nitrogen at  $20^{\circ}$  and 737 mm.  $N = 8.31$ .

0.2036 „ 0.1298  $\text{BaSO}_4$ .  $S = 8.76$ .

$\text{C}_{21}\text{H}_{36}\text{N}_2\text{S}$  requires  $N = 8.04$ ;  $S = 9.19$  per cent.

The thiocarbamide dissolves very readily in alcohol and ethyl acetate, but is insoluble in water and petroleum.



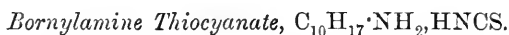
The filtrate from dibornylthiocarbamide was freed from carbon disulphide by evaporation on the water-bath, and the oily residue gradually solidified on cooling. The product was drained on earthenware and extracted with hot petroleum, which left several grams of the thiocarbamide undissolved; the filtrate was evaporated and the residue recrystallised from alcohol until the melting point was constant at  $78^{\circ}$ .

0.2477 gave 15.9 c.c. nitrogen at  $19^{\circ}$  and 763 mm.  $N = 7.41$ .

0.1902 „ 0.2352  $\text{BaSO}_4$ .  $S = 16.98$ .

$\text{C}_{21}\text{H}_{38}\text{N}_2\text{S}_2$  requires  $N = 7.33$ ;  $S = 16.75$  per cent.

The salt melts in hot water without dissolving, but is readily soluble in alcohol, ethyl acetate, and petroleum.



Ninety-five grams of bornylamine hydrochloride were dissolved in water and treated with rather more than the calculated amount of potassium thiocyanate, which immediately formed a white precipitate; sufficient boiling water was added to dissolve the salt, which separated on cooling in the form of long, lustrous needles melting at  $178^{\circ}$ .

0.1664 gave 19.8 c.c. of nitrogen at  $18^{\circ}$  and 762 mm.  $N = 13.78$ .

$\text{C}_{11}\text{H}_{20}\text{N}_2\text{S}$  requires  $N = 13.21$  per cent.

An attempt was made to convert the salt into bornylthiocarbamide  $\text{C}_{10}\text{H}_{17} \cdot \text{NH} \cdot \text{CS} \cdot \text{NH}_2$ . The substance in quantities of five grams was heated at  $180$ — $200^{\circ}$  during one hour, the bubbles of gas appearing at the higher temperature having the odour of ammonia and hydrogen sulphide; the pale brown resin obtained on cooling was insoluble in water and gave no precipitate of bornylamine with alkali. Recrystallisation from absolute alcohol gave lustrous leaflets melting at  $225^{\circ}$ .

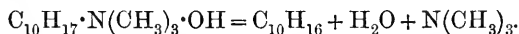
0.1862 gave 13.5 c.c. of nitrogen at 20° and 748 mm.  $N = 8.17$ .

$C_{21}H_{36}N_2S$  requires  $N = 8.04$  per cent.

The substance is therefore dibornylthiocarbamide.

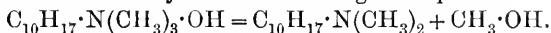
*Trimethylbornylammonium Hydroxide*,  $C_{10}H_{17} \cdot N(CH_3)_3 \cdot OH$ .

It was hoped that by the action of heat on trimethylbornylammonium hydroxide a hydrocarbon might be produced in accordance with the equation



Fifty grams of trimethylbornylammonium iodide were therefore dissolved in water and heated with excess of freshly precipitated silver oxide until the filtrate was free from iodine. On evaporating the colourless liquid, a syrup was obtained which changed in the desiccator to a white, deliquescent solid forming a strongly alkaline solution in water.

This product was transferred to a distilling flask and heated in an air-bath at 200—210°, when a colourless distillate was obtained which separated into two layers. This product, and the residue in the distilling flask, were completely soluble in dilute hydrochloric acid, showing that no hydrocarbon was produced, the decomposition of the substituted ammonium hydroxide following the equation



The dimethylbornylamine obtained in this way boiled at 210—213° under 760 mm. pressure, the platinichloride crystallising in orange needles.

0.1989 gave 0.0505 Pt.  $Pt = 25.38$ .

$(C_{12}H_{23}N)_2 \cdot H_2PtCl_6$  requires  $Pt = 25.19$  per cent.

This attempt to prepare the hydrocarbon having failed, it was thought that the method described by Harries and Antoni (*Annalen*, 1903, 328, 88) might give the desired result. The *hydrogen phosphate* of bornylamine was accordingly prepared by mixing concentrated aqueous solutions of bornylamine hydrochloride (80 grams) and sodium hydrogen phosphate (75 grams); the salt separated immediately in the form of plates, which changed to needles in contact with the mother liquor. The substance is insoluble in alcohol and ethyl acetate, but dissolves readily in water, the dissolved substance undergoing dissociation when boiled. The recrystallised salt was analysed after a few days in the desiccator, as prolonged exposure results in dissociation.

0.2404 gave 14.6 c.c. of nitrogen at 21° and 735 mm.  $N = 6.68$ .

$(C_{10}H_{19}N)_2 \cdot H_3PO_4$  requires  $N = 6.93$  per cent.

On heating the phosphate in an atmosphere of carbon dioxide we again failed to obtain a hydrocarbon, the only product being bornylamine.

ROYAL COLLEGE OF SCIENCE, LONDON,  
SOUTH KENSINGTON, S.W.

## CXXI.—*Halides of the Acridines and Naphthacridines.*

By ALFRED SENIER and PERCY CORLETT AUSTIN.

IN the first memoir published on acridine, Graebe and Caro (1871, *Annalen*, 158, 265) describe a di-iodide of acridine hydriodide, but subsequent inquiry has not increased our knowledge of compounds formed by the addition of halogens to acridines. In the course of further work on these bases, we have observed that such addition takes place readily, giving rise to a series of well-defined crystalline substances. A preliminary account of some of these was communicated to the British Association at the Southport meeting (*Chem. News*, 1903, 88, 273). The compounds are obtained by bringing the halogen into contact with the base, either directly or in solution in an organic solvent; being sparingly soluble in these media they separate immediately, usually in the state of minute crystals, possessing characteristic colours. They are unstable in the presence of water, especially the chlorine compounds and all the compounds derived from acridine itself. The fluorescence exhibited by the acridines when in solution, which depends on the presence of the acridine fluorophore (Jourdan, *Ber.*, 1885, 18, 1447; R. E. Meyer, *Zeit. physikal. Chem.*, 1897, 24, 468), is absent except in three instances.

Chlorine, bromine, and iodine compounds were prepared of the following acridines: acridine, 5-methylacridine, hexamethylacridine,\*  $\alpha$ -naphthacridine (Senier and Goodwin), and  $\beta$ -naphthacridine (Reed). In most instances, the combination took place in the proportion of two atoms of halogen to one molecule of base, but compounds were also obtained containing one, three, or four atoms of the halogen.

Whether these substances are addition or substitution compounds cannot be decided from the results of elementary analysis. That they are not substitution derivatives is shown, however, by their instability,

\* In a paper by Mr. Goodwin and one of us (*Trans.*, 1902, 81, 285), the position of the methyl groups in hexamethylacridine is given according to Graebe's notation as 1:2:4 and 5:6:8. It should be 1:2:4 and 5:7:8 or, according to the notation now generally adopted, 1:3:4 and 6:7:9.

by the small number of halogen atoms which they contain, and by their behaviour with water and alkalis. Instability, which is not generally a character of substitution derivatives, is seen in the fact that, in the presence of water, these compounds decompose, gradually yielding the base and free halogen. In the case of the dichlorine compound of acridine, this was particularly noticed when an attempt was made to prepare a series of salts and double salts in aqueous solutions. These, on analysis, turned out to be salts and double salts of the base itself. Further, this dichlorine compound, the most unstable of the series, was proved to lose chlorine gradually on prolonged exposure to the air. Higher derivatives, too, might be expected if substitution were supposed to take place in the benzene or naphthalene rings for in all the experiments an excess of halogen was employed. That such do not form is seen, notably in the case of the chlorine compound of  $\beta$ -naphthacridine, where only one chlorine atom is found in combination with one molecule of base. Moreover, hexamethylacridine combines with three halogen atoms, although there are only two hydrogen atoms in the benzene rings capable of being replaced. That substitution does not take place in the 5-position in the acridine ring is shown by the fact that on treatment with water or alkalis, acridones are not formed, but the original bases are regenerated. This was proved to be true both of the bromine compound of hexamethylacridine and of the chlorine and bromine compounds of  $\beta$ -naphthacridine.

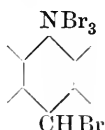
The compounds now being described are therefore regarded as acridine halides or products of the direct addition of halogens to acridines. Moreover, this addition only affects the acridine ring. Were it otherwise, addition could take place only in pairs of atoms, but uneven numbers are found to combine; again, compounds containing a larger number of halogen atoms ought to be formed, for the addition of two monadic radicles to the benzene ring renders further addition easier, a fact usually explained by assuming the disruption of the supposed centric bonds.

Adopting this view, there are two possible monomolecular formulæ available for the dihalides, the acridine ring of which might be thus represented:



The first formula is of the type proposed by Bernthsen and Bender (*Ber.*, 1883, 16, 1802) for the non-fluorescent acridine dihydrides (dihydroacridines) which the dihalides much resemble. This formula is

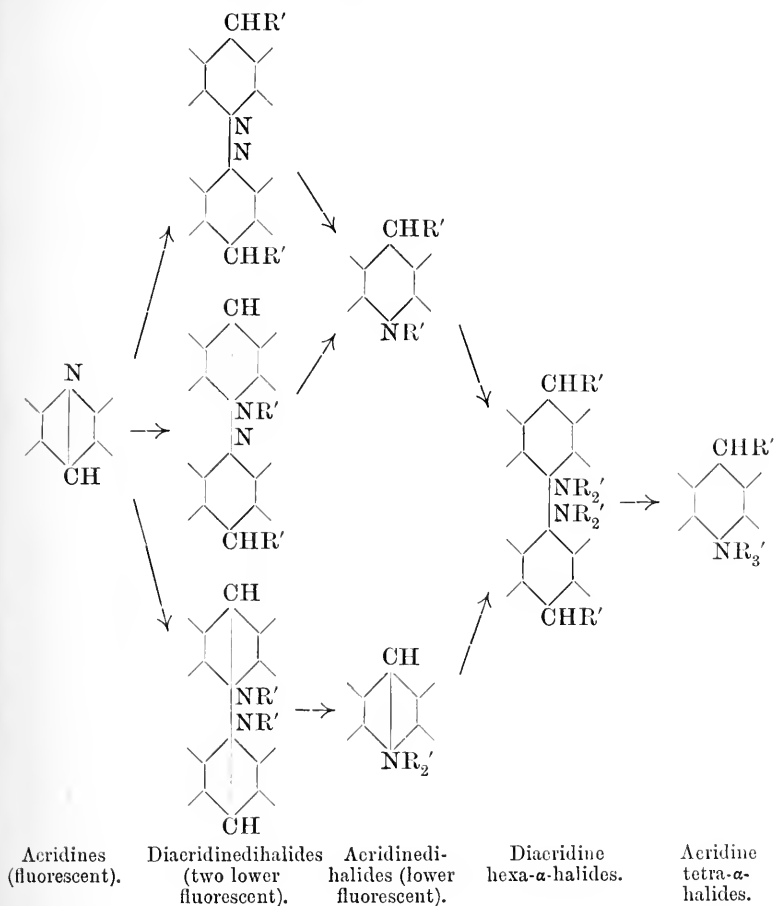
adopted for the non-fluorescent dihalides. The second formula, with its para-linking, showing the acridine fluorophore, is suggested for those dihalides which unmistakably exhibit fluorescence. This formula belongs to the type employed by Bernthsen and Bender for such other di-addition fluorescent compounds as acridinium salts, acridine alkhalides, and acridine alkhydroxides. Several attempts were made, having in view Jourdan's experiments with acridones, to prepare, in presence of catalysts, both these forms from the same base and halogen, and also to convert the one form into the other, but these experiments were not successful. The acridine ring of the one tetra- $\alpha$  halide obtained, a non-fluorescent tetrabromide, can only have the following monomolecular formula :



Now between acridine itself and the dihalides, as also between the dihalides and the tetra- $\alpha$ -halides, intermediate dimolecular compounds may be imagined, which would explain the existence of the products containing one and three atoms of halogen respectively in proportion to one molecule of base. These substances would thus become diacridine dihalides and diacridine hexa- $\alpha$ -halides, and the whole process of halogenation may be represented as shown on p. 1199.

The uppermost dimolecular formula conforms to the type used by Bernthsen and Bender (*Ber.*, 1883, 16, 1971) for Graebe and Caro's "insoluble hydroacridin," and by Graebe and Lagodzinski (*Annalen*, 1893, 276, 35) to explain the constitution of the dimolecular acridone biacridonyl. Recently, also, the middle type has been employed by Möhlau and Haase (*Ber.*, 1902, 35, 4164) for the compound naphth-acrihydridine, the *isonaphthacridine* discovered by Morgan (*Trans.*, 1898, 73, 536).

An interesting relation between these halides and Morgan's *isonaphthacridine* is seen in their behaviour towards acetone. By prolonged boiling with the solvent, they gradually lose their halogen, just as *isonaphthacridine*, when similarly treated, gradually loses hydrogen. When dodecamethylacridine hexabromide is boiled with acetone, it first forms the scarlet dodecamethylacridine dibromide. This scarlet dimolecular acridine dihalide, by further treatment with acetone, is converted by loss of bromine into the monomolecular base, just as, in similar circumstances, Morgan's *isonaphthacridine*, which Möhlau regards as a dimolecular naphthacridine dihydride, is converted by loss of hydrogen into the monomolecular naphthacridine.

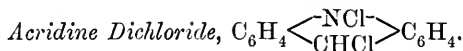


Attempts were made to obtain additional support for these proposed formulæ by determining the molecular weights of the compounds, but their instability and the difficulty of obtaining suitable solvents rendered these unsuccessful.

The compounds described below are mostly insoluble in light petroleum, benzene, toluene, ether, or carbon disulphide, but dissolve in chloroform and glacial acetic acid; in many cases, they are decomposed by acetone. Fluorescence is only regarded as affecting constitution when unmistakably present; for a trace of water in the solvent, or a certain amount of decomposition, often produced a faint fluorescence, which, when greater care was taken, did not appear. The halogen determinations were made by Carius' method, except in the case of the

halides of acridine itself, where it was found preferable to decompose the compounds with alcoholic potassium hydroxide and determine the halogen in this solution.

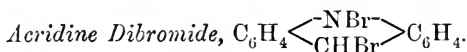
*Acridine Halides.*



A small quantity of acridine was dissolved in dry ether, chloroform, or carbon disulphide, and a stream of dry chlorine introduced until saturation was effected. A canary-yellow precipitate gradually appeared, which soon formed a thick paste; the crystals were filtered off, well-washed with dry ether, and then kept for an hour in a vacuum over potassium hydroxide. The substance may be recrystallised from glacial acetic acid, but it is very unstable, and slowly loses chlorine; it melts at  $240^\circ$  without decomposition. Solutions in glacial acetic acid and chloroform exhibit slight fluorescence, but this is probably due to a decomposition resulting in the separation of acridine.

0.2546 gave 0.2786 AgCl. Cl = 27.04.

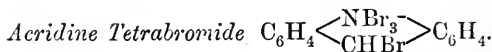
$\text{C}_{13}\text{H}_9\text{NCl}_2$  requires Cl = 28.37 per cent.



A solution of acridine in chloroform was added to excess of a solution of bromine in chloroform, and the yellow precipitate which formed was separated and recrystallised from glacial acetic acid. It does not fluoresce in solution. Its melting point is  $186-188^\circ$ .

0.2388 gave 0.2660 AgBr. Br = 47.4.

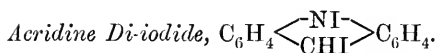
$\text{C}_{13}\text{H}_9\text{NBr}_2$  requires Br = 47.2 per cent.



Acridine was placed in a closed apparatus over bromine and left for two days; the excess of bromine was then removed by spontaneous evaporation, and the residue was well washed with chloroform and finally with ether. No fluorescence was observed. The compound melts with decomposition at  $220^\circ$ .

0.3202 gave 0.4794 AgBr. Br = 63.7.

$\text{C}_{13}\text{H}_9\text{NBr}_4$  requires Br = 64.2 per cent.

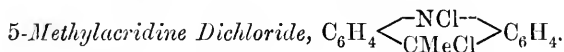


A solution of acridine in chloroform was added to an excess of a solution of iodine in the same solvent, and the precipitate which formed was well washed with dry ether. The crystals, which melt at  $145^\circ$ , are green by reflected light, but no fluorescence could be detected.

0.2858 gave 0.3164 AgI.  $\text{I} = 59.8$ .

$\text{C}_{13}\text{H}_9\text{NI}_2$  requires  $\text{I} = 58.66$  per cent.

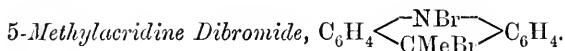
#### 5-Methylacridine Halides.



An excess of dry chlorine was passed into a solution of the base in chloroform, when a bright yellow precipitate slowly separated. As a suitable solvent could not be found, the substance was accordingly well washed with ether and dried in a vacuum over solid potassium hydroxide. It melts with decomposition at about  $280^\circ$ , and its solutions do not exhibit fluorescence until they are very much diluted, when traces could be detected, but this may well be due to decomposition.

0.2149 gave 0.2327 AgCl.  $\text{Cl} = 26.7$ .

$\text{C}_{14}\text{H}_{11}\text{NCl}_2$  requires  $\text{Cl} = 26.8$  per cent.



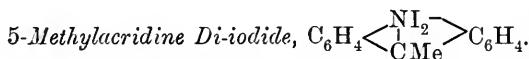
A solution of bromine in chloroform was added in excess to a chloroform solution of the base, when red crystals slowly precipitated; these were washed with ether, separated, and shaken with carbon disulphide until no more bromine could be removed, then washed again with ether and dried in a vacuum over solid potassium hydroxide. The substance decomposes at about  $261^\circ$  without melting. No fluorescence was observed even in very dilute solutions.

0.2293 gave 0.2438 AgBr.  $\text{Br} = 45.24$ .

$\text{C}_{14}\text{H}_{11}\text{NBr}_2$  requires  $\text{Br} = 45.3$  per cent.

The red crystals are nearly insoluble in chloroform, but dissolve in glacial acetic acid, from which, however, they do not crystallise unchanged. Yellow crystals instead are obtained, which were found

to contain a smaller proportion of bromine. Three specimens analysed gave respectively  $\text{Br} = 42.55, 42.9, 40.94$  per cent.

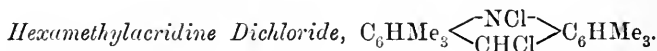


On mixing together concentrated chloroform solutions of the base and iodine containing excess of the latter reagent, dark green needles separated, which were collected, washed with ether, and recrystallised from a little glacial acetic acid. The solution in this solvent is strongly fluorescent, being brownish-red when hot and bluish-green when cold. The substance melts between  $180^\circ$  and  $210^\circ$ .

0.184 gave 0.1906  $\text{AgI}$ .  $\text{I} = 55.9$ .

$\text{C}_{14}\text{H}_{11}\text{NI}_2$  requires  $\text{I} = 56.8$  per cent.

#### *Hexamethylacridine Halides.*



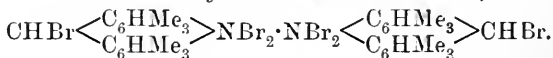
All the materials being carefully dried, a stream of chlorine was passed through some ether in a flask until it was saturated; another portion of ether containing hexamethylacridine, partly in solution and partly in suspension, was slowly dropped into it, the stream of chlorine being continued throughout. A red precipitate gradually separated, which was collected, well washed with ether, and dried in a vacuum.

The compound, which melts at  $216^\circ$ , is soluble in ethyl acetate and acetone, but the latter gradually decomposes it; its solutions show no fluorescence.

0.1595 gave 0.1348  $\text{AgCl}$ .  $\text{Cl} = 20.8$ .

$\text{C}_{19}\text{H}_{21}\text{NCl}_2$  requires  $\text{Cl} = 21.23$  per cent.

#### *Dodecamethyldiacridine Hexabromide,*



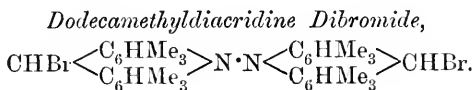
A small quantity of hexamethylacridine was dissolved in chloroform and added to an excess of a solution of bromine in the same solvent. A brown precipitate was obtained, which was washed with ether by decantation and then recrystallised from glacial acetic acid; it consists of brownish-yellow crystals, which show no fluorescence in solution, and melt at about  $287^\circ$ .

0.1581 gave 0.1798  $\text{AgBr}$ .  $\text{Br} = 48.39$ .

$(\text{C}_{19}\text{H}_{21}\text{NBr}_3)_2$  requires  $\text{Br} = 47.70$  per cent.

It was found difficult to remove the last traces of uncombined bromine from this compound, and unless great care was taken the bromine numbers obtained on analysis ranged from 50 to 53 per cent.

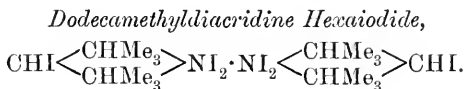
The compound is identical with that described as tribromohexamethylacridine by one of us with Mr. Goodwin (*loc. cit.*), which gave 47.33 per cent. of bromine.



When the brownish-yellow compound last described is boiled with acetone, it undergoes decomposition and becomes converted into a scarlet, crystalline compound with the loss of two-thirds of its bromine. The product is best obtained by boiling the brown compound for about 10 minutes with three successive portions of acetone. In this reaction, hexamethylacridine was found in the acetone washings, showing that part of the hexabromide had lost the whole of its halogen. The dibromide is sparingly soluble in chloroform, but in glacial acetic acid it dissolves more readily than the brown dodecamethylacridine hexabromide. Its solutions do not exhibit fluorescence, and it has no definite melting point.

0.1494 gave 0.0837 AgBr. Br = 23.17.

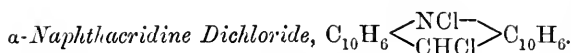
(C<sub>19</sub>H<sub>21</sub>NBr)<sub>2</sub> requires Br = 23.32 per cent.



Chloroform solutions of iodine and hexamethylacridine were mixed, the former in excess, when a precipitate was obtained consisting of brownish-red prisms, which were well washed with ether, dried for 48 hours in a vacuum over solid potassium hydroxide, and finally recrystallised from acetone. The solvent in this instance exerted no decomposing influence; the crystals, which melted at about 275°, exhibited no fluorescence.

0.2059 gave 0.2264 AgI. I = 59.4.

(C<sub>19</sub>H<sub>21</sub>NI<sub>3</sub>)<sub>2</sub> requires I = 59.0 per cent.

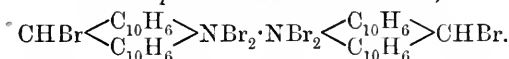
*α-Naphthacridine Halides.*

An excess of dry chlorine was passed into a solution of  $\alpha$ -naphthacridine in carbon disulphide, when the compound separated in small quantity as a bright yellow precipitate. It dissolves in chloroform and is very soluble in glacial acetic acid, but it was not found possible to recrystallise it. It melts indefinitely at about  $158^\circ$ . Its solutions exhibited no trace of fluorescence.

0.2558 gave 0.1900 AgCl. Cl = 18.33.

$C_{21}H_{13}NCl_2$  requires Cl = 20.2 per cent.

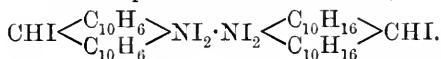
The preparation analysed was not a good one, but there can be no doubt that the compound is a dichloride that had already lost some of its chlorine.

*Di-α-naphthacridine Hexabromide,*

A small quantity of  $\alpha$ -naphthacridine was dissolved in a little chloroform and added to an excess of bromine in ethereal solution. A yellow precipitate was obtained which was recrystallised from glacial acetic acid, the solutions showing no fluorescence. When heated, the compound begins to soften at about  $220^\circ$  and melts with decomposition at  $234^\circ$ . It is insoluble in chloroform and sparingly soluble in glacial acetic acid.

0.1486 gave 0.1584 AgBr. Br = 45.3.

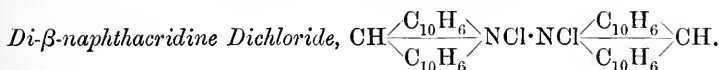
$(C_{21}H_{13}NBr_3)_2$  requires Br = 46.2 per cent.

*Di-α-naphthacridine Hexaiodide,*

Considerable difficulty was experienced in bringing about combination between  $\alpha$ -naphthacridine and iodine. The base, recrystallised from toluene, was dissolved in carbon disulphide and mixed with iodine in the same solvent, when a dark brown, almost black, precipitate was obtained, which was well washed with carbon disulphide, and dried in a vacuum over solid potassium hydroxide. The product dissolves in glacial acetic acid; the solution is not fluorescent.

0.2168 gave 0.2322 AgI. I = 57.87.

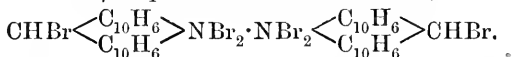
$(C_{21}H_{13}NI_3)_2$  requires I = 57.7 per cent.

*β-Naphthacridine Halides.*

About half a gram of Reed's *β*-naphthacridine was dissolved in a little chloroform and the solution dropped slowly into a saturated solution of chlorine, in chloroform, through which chlorine was passing. A bright yellow, crystalline compound was formed, which when recrystallised from glacial acetic acid, separated in pale yellow needles. The crystals, which give strongly fluorescent solutions, do not melt below 300°.

0.2578 gave 0.1113 AgCl. Cl = 10.8.

$(\text{C}_{21}\text{H}_{13}\text{NCl})_2$  requires Cl = 11.26.

*Di-β-naphthacridine Hexabromide,*

To an ethereal solution of bromine was added about 0.25 gram of Reed's *β*-naphthacridine dissolved in chloroform. A voluminous yellow precipitate appeared which was separated, well washed with ether, and dried in a vacuum over solid potassium hydroxide. Traces of fluorescence were observed in the chloroform and glacial acetic acid solutions, but these were probably due to admixture with the base. The compound had no definite melting point.

0.1310 gave 0.1450 AgBr. Br = 47.1.

$(\text{C}_{21}\text{H}_{13}\text{NBr}_3)_2$  requires Br = 46.2 per cent.



A chloroform solution of Reed's *β*-naphthacridine was added to a cold, nearly saturated solution of iodine in the same solvent. A dark precipitate formed which was separated, washed well with ether, and recrystallised from glacial acetic acid, when it left a small, black residue. The solution yielded dark green crystals, which melt at 270—273° after softening at about 260°. The solution in glacial acetic acid is strongly fluorescent.

0.1375 gave 0.1184 AgI. I = 46.5.

$\text{C}_{21}\text{H}_{13}\text{NI}_2$  requires I = 47.65 per cent.

Another analysis gave I = 51.02 per cent.

Our thanks are due to Mr. William Goodwin and Miss F. M. G. Micklethwait for valuable help rendered during the early part of this inquiry.

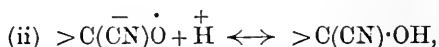
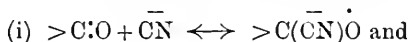
QUEEN'S COLLEGE,  
GALWAY.

CXXII.—*Reactions Involving the Addition of Hydrogen Cyanide to Carbon Compounds. Part II. Cyanohydrins Regarded as Complex Acids.*

By ARTHUR LAPWORTH.

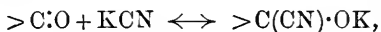
IN a recent communication (Trans., 1903, 83, 995) the effect of catalytic agents on the velocity of addition of hydrogen cyanide to carbon compounds was described, and it was shown that the observations could best be accounted for on the assumption that the process occurs in two stages; the initial stage was supposed to consist in the formation of a complex cyanide ion, the subsequent union of these with hydrogen ions affording the synthetical products.

In the simplest case, namely, where the addition occurs at a carbonyl group, the hypothetical process was represented by:



a process involving the conclusion that the cyanohydrins are acidic in character. Although from other considerations this appeared in the highest degree probable, since these compounds are cyano-derivatives of alcohols, and should therefore be more markedly acidic than the latter, which form metallic derivatives, no direct proof of the acidic character of the cyanohydrins was brought forward.

In attempting partially to reconcile the idea with prevailing views on organic compounds, it was remarked that the accelerating influence of bases in promoting the additions of hydrogen cyanide might temporarily be regarded as the result of the initial addition of a salt of the acid, thereby affording a salt of the cyanohydrin; thus, with potassium hydroxide as the base,



with the reservation that this explanation applies to one side of the question only.

Regarded from either standpoint, the conception involves (1) that the cyanohydrins are acidic in character, and (2) that their salts are formed, although possibly only to a minute extent, when hydrogen cyanide, for example, in presence of bases or potassium cyanide, reacts with the carbonyl compounds.

It must be made clear that there is no trustworthy process of reasoning whereby their degree of acidity might be foretold, but it is natural to surmise that they should be more acidic than the saturated fatty alcohols. The application of the theory of Abegg and Bodländer (*Zeit. anorg. Chem.*, 1899, 20, 475) to the case may appear at first sight to be straightforward, as, according to this view, the complex ion should have a greater capacity for the negative charge than the simple one, hence the cyanohydrins should be more powerful acids than  $\text{H}\cdot\text{C}:\text{N}$ . There are, however, several reasons which render it impossible to attach any confidence to this mode of reasoning—firstly, because it is not yet possible to guess, even approximately, the affinity of  $\text{H}\cdot\text{C}:\text{N}$ , in the absence of precise knowledge as to the nature of a solution of hydrogen cyanide in water owing to the exhibition of tautomerism, and, secondly, it is doubtful whether it will be found possible to maintain the universal correctness of the above-mentioned principle. In regard to the latter point, it seems reasonable to suppose, if indeed it is not highly probable, that the phenomena attending the electrolysis of complex electrolytes may frequently be the result of the breaking down of the complex ions after discharge, rather than the selective discharge of simple ions which may or may not be present in appreciable amounts. The potential of the complex ion may conceivably be greatly influenced by its configuration so as to rise even above that of the simple ion, and this appears more likely to occur when the “free affinity” of the complex ion is transferred to a point on the neutral component, as is perhaps usually the case, and is undoubtedly so in the foregoing instance.

The work described in the present communication was carried out with the object of ascertaining whether, in presence of excess of potassium cyanide, the additive products of that salt with carbonyl compounds could be isolated; secondly, to determine whether these products are electrolytes, in which case the complex ions of the type previously assumed must certainly exist; and, lastly, to gain a rough idea as to the relative affinities, as acids, of hydrocyanic acid and the cyanohydrins.

It was found that crystalline products could be prepared by the direct action of potassium cyanide on benzaldehyde and camphorquinone, and that these products have approximately the composition of hydrated potassium salts of the corresponding cyanohydrins, the

divergence probably originating in the fact that it was not found possible to recrystallise them except from solutions which contain considerable quantities of the products of hydrolytic and molecular dissociation.

So far as could be ascertained, these compounds behaved consistently, as should be anticipated on the assumption that they are electrolytes which, on dissolution in water, afford the complex cyanide ion,  $\text{CN} \cdot \text{CR}_1\text{R}_2 \cdot \text{O}^-$ , of the cyanohydrins, which must therefore be distinctly acidic in character. Attempts to estimate the approximate affinities of the cyanohydrins were only partially successful, but it seems quite clear that they are much weaker than the ordinary phenols, and their salts must be hydrolytically dissociated to a very considerable extent; further, the presence of water determines the decomposition of the salts into potassium cyanide and the carbonyl compound from which they are derived.

The whole of the evidence, then, tells in favour of the view which has been advanced as to the mechanism of the action of hydrogen cyanide on carbonyl compounds. The most important point in that theory, namely, that the complex ion formation precedes that of the cyanohydrin or its salt, is advantageous because of its greater simplicity (compare *Trans.*, 1903, 83, 1001) as compared with the opposite view, as it involves the union of two instead of three individuals, and, moreover, explains the observation that acids greatly retard the union of camphorquinone with hydrogen cyanide in aqueous solution, even when care is exercised to employ materials free from traces of impurities of a basic nature, the presence of which would tend to vitiate the conclusion drawn. It is to be hoped that before long it may be found possible by measurements of the reaction velocities in this or in similar cases to throw further light on this most important question.

#### EXPERIMENTAL.

##### *The Potassium Cyanide Derivative of Benzaldehyde,*



It was shown in the previous communication (*loc. cit.*, p. 1003) that when benzaldehyde is shaken at the ordinary temperature with an aqueous solution of hydrogen cyanide, an unexpectedly large quantity of the cyanohydrin is formed; if special precautions are taken, still more interesting results are obtained.

When hydrogen cyanide was passed into an ice-cold solution of potassium hydroxide containing benzaldehyde in suspension, it was noticed that the opalescent liquid became almost transparent at a

certain stage, and subsequently returned to its original opaque condition. This suggested that the hypothetical potassium salt of the cyanohydrin was more stable than at first supposed, and attempts to isolate it were therefore instituted.

If an ice-cold saturated solution of potassium cyanide is added gradually to benzaldehyde, also at  $0^{\circ}$ , with constant stirring, a milky emulsion is at first produced, but this quickly becomes clear and homogeneous. If the vessel is removed from the cooling mixture, it gradually becomes opaque once more, and so sensitive is the solution to rise of temperature that if the hand is applied to the sides of the vessel, local decomposition is caused. The oil which separates under these conditions was found to be a mixture of benzaldehyde and its cyanohydrin.

If an excess of saturated potassium cyanide solution is added to the clear liquid obtained as above, and the solution left at  $0^{\circ}$ , a white, crystalline salt separates, the formation of which is promoted by scratching the sides of the vessel, and the whole may become semi-solid.

The material may be separated by filtration, and as it was found impossible to recrystallise it in the ordinary way, it was prepared for analysis by spreading it in a very thin layer over highly absorbent earthenware, which was subsequently placed beneath a bell-jar together with a vessel containing an alkali hydroxide to remove carbon dioxide. The dry salt was afterwards washed with a little ice-cold water, dried over sulphuric acid and potassium hydroxide in a vacuum, and finally washed with dry chloroform, which was removed by exposure over solid paraffin.

A specimen prepared in the above way was analysed, the total carbon being estimated by combustion in a tube containing lead chromate, and then continuing the process after the addition of some finely divided silica to the residue in the boat. The water of crystallisation could not be estimated directly, as the substance decomposed rapidly at temperatures considerably below  $100^{\circ}$ . The cyanogen was estimated by adding excess of a decinormal solution of silver nitrate to a weighed quantity of the salt dissolved in water, and determining the excess of silver after acidifying with nitric acid.

0.3458 gave 0.1371  $K_2SO_4$ .  $K = 17.8$ .

0.7672 „ 0.3050  $K_2SO_4$ .  $K = 17.9$ .

0.4748 required 23.05 c.c.  $N/10$   $AgNO_3$ .  $CN = 12.6$ .

0.4171 gave 25.45 c.c. nitrogen at  $16^{\circ}$  and 747 mm.  $N = 6.8$ .

0.2392 „ 0.3856  $CO_2$  and 0.1072  $H_2O$ .  $C = 43.9$ ;  $H = 5.0$ .

$C_7H_6O, KCN, 2\frac{1}{2}H_2O$  requires  $K = 18.1$ ;  $CN = 12.0$ ;  $C = 44.4$ ;  $H = 5.1$ ;  
 $N = 6.5$  per cent,

The amounts of potassium and cyanogen in a number of other specimens were estimated and found to vary considerably, but were in most cases nearly in equivalent proportions. Thus it seems unquestionable that the substance is an additive product of the aldehyde with potassium cyanide with an uncertain quantity of water, probably less than  $2\frac{1}{2}$  molecular proportions.

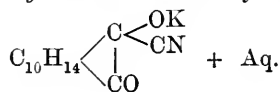
The salt forms thin, rectangular plates which have straight extinction, and probably belong to the orthorhombic system; it dissolves readily in ice-cold water, but is partially decomposed and a milky liquid results; if some potassium cyanide is present, however, a clear solution may be obtained: this, when warmed, becomes opalescent. It dissolves in strong alcohol, and on adding benzene a deposit of glistening plates is obtained; these, however, consist of pure potassium cyanide. As was to be anticipated from the latter observation, potassium cyanide dissolves somewhat freely in 95 per cent. alcohol containing benzaldehyde, although it is very sparingly soluble in pure alcohol of that strength.

The salt is very stable towards chloroform or benzene, but if washed with moist ether it is slowly decomposed, and potassium cyanide, nearly free from benzaldehyde, remains.

On exposure to a moist atmosphere containing carbon dioxide, the compound becomes sticky, and is finally converted into a mixture of potassium carbonate, mandelonitrile, benzaldehyde, and benzoin, the whole appearing reddish-brown. If, however, the substance is kept in a desiccator over an alkali hydroxide and sulphuric acid, it may be preserved with little alteration for some weeks or months.

An aqueous solution of the substance is decomposed by very weak acids, such as hydrocyanic acid and even phenols, the free cyanohydrin being deposited as an oil.

*The Potassium Cyanide Derivative of Camphorquinone,*



Camphorquinone forms a very well defined additive product with potassium cyanide, which may be prepared as follows.

An ice-cold, nearly saturated, solution of potassium cyanide is gradually added to the quinone, which is contained in a mortar and constantly triturated. The yellow powder gradually becomes replaced by a white, potassium salt, which may be transferred to a porous plate, dried over sulphuric acid and an alkali hydroxide, and washed with a considerable amount of chloroform to remove unaltered quinone. It is perhaps more satisfactory, however, to add the requisite amount of

potassium cyanide dissolved in water to the quinone, finely powdered and suspended in its own weight of alcohol; in this case, the powder first dissolves to a nearly colourless solution, and finally separates in the form of the additive product.

The method which gave the best products was the following: the quinone was dissolved in chloroform, and to the solution was added a moderately strong solution of potassium cyanide in excess, the whole being finally cooled to  $0^{\circ}$ , when it became colourless, and eventually the solid compound separated in well-formed crystals, and was purified and dried in the manner previously indicated.

The compound is more stable than that of benzaldehyde, and may be recrystallised by dissolution in ice-cold water containing a small quantity of potassium cyanide, and allowing the filtered solution to evaporate in a vacuum over sulphuric acid; it is very doubtful, however, if any real advantage is thereby gained.

A specimen prepared by the second of the above methods was analysed.

0.1675 gave 0.0522  $K_2SO_4$ .  $K = 13.9$ .

0.4077 „ 0.1254  $K_2SO_4$ .  $K = 13.8$ .

0.4402 required 16.3 c.c.  $N/10$   $AgNO_3$ .  $CN = 9.6$ .

0.1676 gave 0.2818  $CO_2$  and 0.1211  $H_2O$ .  $C = 45.8$ ;  $H = 8.0$ .

$C_{10}H_{14}O_2, KCN, 3H_2O$  requires  $K = 13.7$ ;  $CN = 9.3$ ;  $C = 46.3$ ;  $H = 7.7$  per cent.

The approximate agreement of the analytical results with the formula suggested is probably accidental. A considerable number of specimens, prepared in various ways, were analysed, and gave varying results. Three specimens gave respectively (a)  $K = 16.4$ ,  $CN = 10.2$ ; (b)  $K = 12.9$ ,  $CN = 9.1$ ; (c)  $K = 13.7$ ,  $CN = 10.1$  per cent. As a general rule, the ratio  $K : CN$  was somewhat too low, suggesting that some free cyanohydrin was present. In all cases, the specimens analysed were free from colour, and therefore from unaltered camphorquinone.

The salt crystallised in thin, usually four-sided, rectangular plates having straight extinction. It may be dissolved, with care, in ice-cold water, affording a clear, colourless solution, which, when warmed, becomes yellow and finally turbid at a temperature which depends on the concentration. A very small quantity of potassium cyanide raises the temperature at which this takes place. If the yellow solution is shaken with ether, the latter is found to extract a mixture of camphorquinone and its cyanohydrin (compare Trans., 1903, 83, 1003). If carbon dioxide or hydrogen cyanide is passed into the clear, aqueous solution, a turbidity at once appears, and a colourless oil is finally obtained; this is found to be nearly pure camphorquinone cyano-

hydriin, as it affords an excellent yield of the corresponding amide on treatment with fuming sulphuric acid (*loc. cit.*).

A portion of the specimen the analysis of which is given above was sent to Prof. James Walker, who kindly undertook some measurements of the conductivity of its solution in water, alone and in presence of potassium cyanide. He reports: "It is difficult to interpret the results owing to the possibility of the occurrence of several kinds of hydrolysis. The conductivity of potassium cyanide falls on combination with camphorquinone to an extent which cannot be accounted for solely on the assumption that the negative complex ion has a very small velocity of migration and the fall is greater for the first  $\frac{1}{2}$  molecule of the quinone than for the second. It is therefore clear that a diminution in the amount of ionisation must have taken place; nevertheless, in my opinion, the new compound is a moderately good electrolyte."

*Affinity of the Cyanohydrins as Acids.*—A considerable number of attempts were made to obtain a satisfactory comparison of the affinities of the cyanohydrins with that of hydrocyanic acid. Qualitative experiments showed that on adding a reactive ketone or an aldehyde to an aqueous solution of potassium cyanide containing free hydrocyanic acid and coloured with phenolphthalein, an increase in the red colour was always produced. This observation indicated that the solution became more strongly alkaline, but might be accounted for by the existence of an unstable compound of the phenolphthalein with hydrocyanic acid, the concentration of which would be diminished on the partial removal of hydrocyanic acid from the solution by the ketone or aldehyde.

Efforts were now made to compare the speeds with which relatively small quantities of ethyl formate are hydrolysed by aqueous solutions of potassium cyanide, alone and with the addition of ketones and aldehydes. In the former case, by removing portions of the reaction mixture, diluting largely with ice-cold water, precipitating the cyanide by addition of silver nitrate, and finally removing the latter by sodium chloride, sharp results could be obtained on titration with standard alkali; in presence of aldehydes and ketones, however, the numbers were not so concordant, but in every case it was found that the apparent end point in the hydrolysis was reached much more rapidly when benzaldehyde or camphorquinone was present, indicating a greater initial alkalinity in the presence of the carbonyl compound.

Another mode of investigation was also adopted, namely, a direct comparison of the cyanohydrin,  $\text{CN} \cdot \text{CMe}_2 \cdot \text{CH}_2 \cdot \text{CMe}(\text{OH}) \cdot \text{CN}$ , with  $\beta$ -naphthol, as regards the effect of alkali on their solubilities in water. This cyanohydrin was chosen on account of its relatively

great stability, and because its equivalent is nearly the same as that of  $\beta$ -naphthol.

0.0460 gram of the cyanohydrin dissolved without difficulty and within 3 minutes in 15 c.c. of water at  $16^{\circ}$ , whilst the same weight of  $\beta$ -naphthol did not dissolve in 50 c.c. of water at that temperature after 4 days. This weight of each of these compounds was then covered with 1 c.c. of water, and the smallest amount of  $N/10$  sodium hydroxide required to bring them completely into solution was determined. It was found that 5.8 c.c. were required for the cyanohydrin, and 6.3 c.c. for the naphthol (the equivalent volume of the alkali is 3.0 c.c. in each case). Hence, whilst the cyanohydrin is very much more readily soluble in water, the excess of soda required to keep the substance in solution at a concentration approximately about  $N/20$  is not very different in the two cases. It may safely be concluded, therefore, that this cyanohydrin is a much weaker acid than  $\beta$ -naphthol, and therefore *a fortiori* than hydrocyanic acid.

Numerous aldehydes and ketones besides the two above dealt with were investigated, in the hope of being able to obtain from them similar potassium cyanide additive compounds, but with indifferent success.

In the case of fatty aldehydes, no solid salts were isolated, but it was frequently found that the aldehydes were more readily soluble in ice-cold potassium cyanide solution than in water; heat was generated, and in many cases condensation of the aldehyde took place to some extent. The nitrobenzaldehydes reacted very rapidly, but secondary reactions occurred.

Both *o*- and *p*-bromobenzaldehydes dissolved very rapidly in concentrated potassium cyanide solutions and gave clear solutions at the ordinary temperature, so that the additive compounds are apparently more stable than that of benzaldehyde itself: this is perhaps what might be anticipated, as the tendency to the formation of negative complex ions should, other things being equal, increase with the "negativeness" of the neutral component. Colourless, crystalline compounds were isolated from these solutions, but these can scarcely be of a simple character, as they contained only about one-half the required proportion of potassium, the proportion of cyanide being comparatively high; this suggests that they were mixed with free cyanohydrins.

Saturated fatty and aromatic monoketones did not appear to dissolve in ice-cold potassium cyanide to any marked extent; moreover, their cyanohydrins, which are very easily obtained if acid is added, were rapidly decomposed by ice-cold alkalis. Their behaviour suggests that the aldehydes differ from the ketones mainly in that they yield more stable additive compounds, rather than that they afford them

more readily; that is to say, the velocity of the breaking down of the complex ion as compared with that of its formation is, in these cases, relatively high.

The author's thanks are due to the Research Fund Committee of the Chemical Society for a grant which defrayed part of the cost of this investigation.

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CXXIII.—*Reactions Involving the Addition of Hydrogen Cyanide to Carbon Compounds. Part III.*  
*Action of Potassium Cyanide on Mesityl Oxide.*

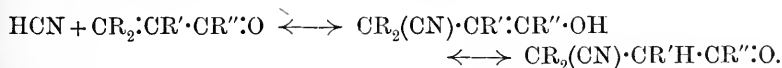
By ARTHUR LAPWORTH.

It is well known that the ethylenic linking in  $\alpha\beta$ -unsaturated ketones, aldehydes, and esters is characterised by an exceptional reactivity, and these compounds are capable of taking up at the carbon double bond, not only agents with which ordinary unsaturated compounds unite, such as the halogens or the halogen hydrides, but also a number of those which otherwise exhibit additive functions only in respect to the carbonyl group, that is to say, agents such as hydroxylamine, sodium hydrogen sulphite, and ammonia. Further, it is frequently the case that the carbonyl group of an  $\alpha\beta$ -unsaturated ketone or aldehyde appears devoid of reactivity until addition has first occurred at the ethylenic position, or, if a reactive character is manifested, it is usually less marked than in the corresponding saturated compounds.

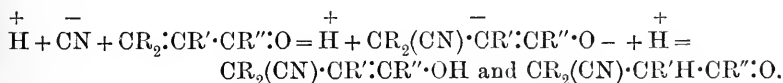
Addition in this class of compounds is governed by the law that the negative part of the agent added is taken up at the  $\beta$ -position, hence where an acid or other hydrogen compound is added in two parts, for example, H and  $\text{NH}_2$ , H and Cl, H and  $\text{NH}\cdot\text{OH}$ , H and  $\text{CH}(\text{CO}_2\text{Et})_2$ , the product contains the hydrogen in the  $\alpha$ -position.

Whilst it is too early to discuss in great detail the theory of the addition process in these compounds, it may be worth while to point out that the conditions under which these additions occur are precisely similar to those which are advantageous in the case of simple carbonyl compounds. One very favourable condition appears to be a high concentration of the negative ion of the agent, as is particularly noticeable in the case of hydrogen cyanide addition processes (Trans., 1903,

83, 997). Hence it is natural to surmise that the principle which appears to be one of the governing factors in the simpler cases applies to the other, namely, the formation of a complex negative ion as an initial step. If so, then it should follow that, other things being equal, the greater the affinity of the resulting complex ion for the negative charge, the greater should be the tendency towards the complex formation, or, in other words, the more acidic the character of the compound first formed, the more readily should the synthetical process occur, when this change consists in the addition of a hydrogen compound in the above sense. Now, in accordance with Thiele's theory of such additions, the initial compound is to be regarded as the enol, and therefore a substance of distinctly acidic character :



A simple modification of this gives the ionic view :



Such a modification of Thiele's theory appears likely to afford the basis of a rational explanation of the great difference in reactivity between the groups  $\text{>C:C<}$  and  $\text{>C:}\dot{\text{C}}\text{:}\dot{\text{C}}\text{:C<}$ , on the one hand, and  $\text{>}\dot{\text{C}}\text{:O}$  and  $\text{>C:}\dot{\text{C}}\text{:}\dot{\text{C}}\text{:O}$ , on the other, for the same assumptions applied to the former class would lead to the formulation of additive products,  $\text{>CX-CH<}$  and  $\text{>CX:}\dot{\text{C}}\text{:}\dot{\text{C}}\text{:CH<}$ , that is to say, groups of a type with which acidity has not yet been definitely associated.

Of the addition reactions in which these  $\alpha\beta$ -unsaturated compounds take part, some have proved of great value as general synthetical methods, in particular those which involve the union of a carbon atom with the  $\beta$ -carbon atom of the unsaturated compound. Such, for example, are the reactions with ethyl malonate and ethyl acetoacetate, which lead to the production of substituted glutaric acids,  $\delta$ -ketocarboxylic acids, or dihydroresorcinols.

Numerous attempts have probably been made to discover a general method by which the addition of the elements of hydrogen cyanide at the double linking in  $\alpha\beta$ -unsaturated ketones, &c., might be brought about, but hitherto with only partial success. Bredt and Kallen (*Annalen*, 1896, 293, 350) were unable to bring about the interaction of  $\alpha\beta$ -unsaturated monocarboxylic acids or esters with hydrogen cyanide, but discovered that if the esters of alkylidenemalononic acids were dissolved in dilute alcohol containing potassium cyanide, and the mixture was then treated with acid or warmed at about  $80^\circ$ , so as to

cause partial hydrolysis of the ester and consequent liberation of hydrogen cyanide, the desired additive products were obtained; the efficiency of the method was attributed to a special property of nascent hydrogen cyanide.

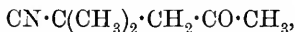
In a recent paper (Trans., 1903, 83, 995), the author showed that hydrogen cyanide is much more efficient as an additive reagent when its own salts are present, and described methods of bringing about the addition of that agent at the double linking in an  $\alpha\beta$ -unsaturated ketone (phorone) and an  $\alpha\beta$ -unsaturated nitrile (benzylidenebenzylcyanide). It was shown also that these compounds actually remove hydrogen cyanide from the alkaline solution of potassium cyanide (*ibid.*, 1003).

The extraordinary ease with which the addition was thus effected naturally led to a more systematic investigation of the reaction, with the result that it proves likely to be an important systematic method, and perhaps may be so developed as to afford a fairly convenient process for preparing  $\gamma$ -ketonic nitriles and acids, 1:2-dinitriles, and substituted succinic acids.

Unfortunately, however, potassium cyanide, which usually must be present in considerable quantity, is only very sparingly soluble in alcohol, except in presence of much water, so that the resulting alkaline solutions tend to cause by-reactions; it is therefore desirable that a considerable number of cases should be somewhat thoroughly investigated, so as to determine the conditions most suitable for the treatment of compounds of different types.

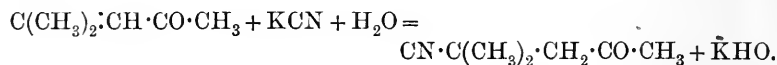
No difficulty was found with phorone or benzylidenebenzyl cyanide, because the products are stable and crystallise very easily, but a number of other cases which have since been attacked have given much trouble. In this paper, some of the results obtained with mesityl oxide,  $\text{C}(\text{CH}_3)_2\cdot\text{CH}\cdot\text{CO}\cdot\text{CH}_3$ , are described.

The conversion of acetone into mesitononitrile,



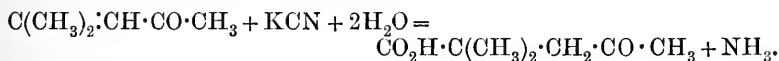
was first effected by Pinner (*Ber.*, 1881, 14, 1072), who saturated the ketone with hydrogen chloride and heated the product with a solution of potassium cyanide.

It is most probable that the process occurs in two stages, the first of which involves the formation of water and mesityl oxide, followed by the interaction of the latter with potassium cyanide and water, thus,

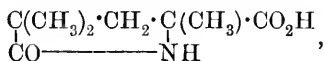


In accordance with this view, it has now been found that mesityl oxide, like phorone (Trans., 1903, 83, 1003), when heated with a dilute

alcoholic solution of potassium cyanide, alone or in presence of free hydrogen cyanide, reacts in the above way, as the solution becomes strongly alkaline, and the product when poured into water and hydrolysed with hydrochloric acid yields mesitonic acid; after 10 minutes' heating on the water-bath, more than half the ketone is converted into mesitononitrile and other substances. If the heating be prolonged, the potassium hydroxide liberated in the reaction hydrolyses the nitrile formed, yielding the corresponding carboxylic acid, so that in one operation the synthesis of a  $\gamma$ -ketonic acid from an  $\alpha\beta$ -unsaturated ketone is accomplished,

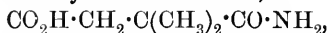


Not only is it possible so to prepare the  $\gamma$ -ketonic acid, but the reaction proceeds even further. The mononitrile first formed readily affords a somewhat stable cyanohydrin, which is probably formed in appreciable amount in the alkaline solution, because at the end of an operation in which the ketone had been boiled for a considerable time with the cyanide solution, mesitylic acid,



was obtained on acidification, and this must have been formed from the cyanohydrin of mesitononitrile or from mesitonic acid itself.

The constitution of mesitylic acid has already been satisfactorily determined by Pinner (*Ber.*, 1881, 14, 1075, and 1882, 15, 582), who obtained from it *as*-dimethylsuccinamic acid,



by the oxidising action of potassium permanganate in acid solution; moreover, as he found it yielded mesitonic acid when it is heated with sulphuric acid at  $150^\circ$  (*Ber.*, 1882, 15, 585), the constitution of the ketonic acid was scarcely questionable. When mesitonic acid is oxidised with nitric acid, however, it yields dimethylmalonic acid, whilst dimethylsuccinic acid does not appear to have been detected. In order to obtain this acid and at the same time to establish conclusively the view that the ketonic acid contains the group  $\cdot\text{CO}\cdot\text{CH}_3$ , mesitonic acid, prepared by the new process, was oxidised by means of warm dilute sodium hypobromite. As was to be anticipated, bromoform and *as*-dimethylsuccinic acid were obtained without difficulty.



In agreement with the supposed ketonic nature of mesitonic acid, it yields an oxime, a semicarbazone, and hydrazones, all having well-defined crystalline habits.

The results, taken in conjunction with the work of Bredt and Kallen (*loc. cit.*), and the author's observations on benzylidenebenzyl cyanide, show that the addition of hydrogen cyanide to unsaturated compounds containing the group  $\text{:C}:\dot{\text{C}}\cdot\text{R}$  (where  $\text{R} = \cdot\text{CO}\cdot$  or  $\text{CN}$ ) occurs in accordance with the usual rule.

## EXPERIMENTAL.

### *Action of Potassium Cyanide on Mesityl Oxide.*

In preliminary experiments made with the object of bringing about the addition of one molecular proportion of hydrogen cyanide to mesityl oxide, the ketone was shaken with an aqueous solution of potassium cyanide containing one molecular proportion of free hydrogen cyanide. Occasionally it occurred that, after some days, the liquid ketone was replaced by a relatively small quantity of a solid, crystalline material, which on examination proved to consist of the cyanohydrin of mesitonenitrile, but the yield obtained by this method was exceedingly poor, and various modifications of the method were therefore tried. The results generally tended to show that much of the difficulty arose from the circumstance that the mesitonenitrile initially formed reacted much more rapidly with the reagent than did the original mesityl oxide.

As, however, the ketone-cyanohydrins are usually easily broken down by alkali, whilst the  $\gamma$ -cyanoketones are comparatively stable, experiments were next instituted with the object of ascertaining what would be the result if potassium cyanide alone were employed, since in this case the alkali formed by the removal of the elements of hydrogen cyanide from the solution in the initial stage might be expected to prevent the formation of a cyanohydrin. Thus 3.9 grams of the ketone (1 mol.) were dissolved in 25 c.c. of alcohol and warmed on the water-bath with a solution of 5 grams of potassium cyanide (2 mols.) in 15 c.c. of water. Within a few minutes the odour of ammonia was noticed, and at the end of an hour the whole was evaporated on the water-bath to drive off alcohol, the residue being diluted with water and extracted repeatedly with ether. On evaporating the ethereal extracts, practically no residue was obtained; the aqueous liquid was therefore strongly acidified and the extraction with ether repeated, when the ethereal extracts now yielded a considerable residue; this was found to consist of a portion, easily soluble in water, which was mainly mesitonic acid, whilst the less soluble portion was crystalline, and was identical with mesitylic acid. These substances had evidently resulted from the addition of one and two

molecular proportions of hydrogen cyanide to the mesityl oxide, followed by hydrolysis of the products in the alkaline liquid.

The experiments indicated that the addition process in solutions of the concentrations employed was somewhat rapid at the temperature of the water-bath, and it was therefore possible to devise methods for obtaining any one of the products at will. The precise conditions which were finally adopted in each case are given below.

*Preparation of Mesitonic Acid*,  $\text{CO}_2\text{H}\cdot\text{C}(\text{CH}_3)_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_3$ .

In preparing this substance, a solution of mesityl oxide (1 mol.) in six times its weight of boiling alcohol is mixed with a solution of potassium cyanide (2 mols.) in three times its weight of hot water, and the whole heated on the water-bath during 15 minutes. To the cooled liquid is then added an aqueous solution of ferrous sulphate ( $\frac{1}{3}$  mol.), which serves the purpose of converting excess of potassium cyanide into ferrocyanide as well as decomposing any cyanohydrin formed. The latter process is completed by raising the whole once more to the boiling point with constant shaking, care being taken that the liquid remains alkaline throughout. After filtration through glass wool, the liquid is diluted largely with water, extracted with ether, the ethereal extract being dried with calcium chloride and evaporated. The liquid residue, which is mainly mesitonitrile, is dissolved in hydrochloric acid (saturated at  $0^\circ$ ), the whole being allowed to remain for two days in the cold, after which it evaporated on the water-bath. The oily acid remaining is best purified by dissolving it in ethyl bromide, the solution being dried with calcium chloride. By adding light petroleum to the liquid and allowing the whole to evaporate spontaneously, the product may be obtained without further difficulty in quadrangular plates or magnificent, transparent rhombs which are nearly pure mesitonic acid. The acid is easily obtained in a purified condition by recrystallisation from the same mixture.

0.3003 gave 0.6392  $\text{CO}_2$  and 0.2322  $\text{H}_2\text{O}$ .  $\text{C} = 58.0$ ;  $\text{H} = 8.6$ .

$\text{C}_7\text{H}_{12}\text{O}_3$  requires  $\text{C} = 58.3$ ;  $\text{H} = 8.3$  per cent.

The acid had all the properties assigned it by Pinner (*Ber.*, 1881, 14, 1072, and 1882, 15, 585); it melted at  $75.5$ — $76.5^\circ$  and crystallised by careful evaporation of its solution in a mixture of ethyl bromide and light petroleum in magnificent, transparent rhombs which have one plane of perfect cleavage.

When fused on a microscopic slide beneath a cover-glass, it solidified somewhat rapidly, forming semi-transparent patches which show aggregate extinction. Examination of the mass in convergent, polar-

ised light reveals, here and there, the interference figure surrounding the bisectrix of a biaxial crystal of very wide axial angle; if, as is probable, this is the obtuse bisectrix, the double refraction is positive in sign and strong.

The following new derivatives of the acid were prepared with the object of more fully characterising the compound.

The *semicarbazone*,  $\text{CO}_2\text{H}\cdot\text{C}(\text{CH}_3)_2\cdot\text{CH}_2\cdot\text{C}(\text{CH}_3):\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ , is rapidly deposited on warming an aqueous solution of the acid with semicarbazide acetate; it was purified by crystallisation from dilute ethyl alcohol. On analysis of the material dried at  $100^\circ$ :

0.1982 gave 0.3468  $\text{CO}_2$  and 0.1335  $\text{H}_2\text{O}$ .  $\text{C} = 47.7$ ;  $\text{H} = 7.5$ .

$\text{C}_8\text{H}_{15}\text{O}_3\text{N}_3$  requires  $\text{C} = 47.7$ ;  $\text{H} = 7.7$  per cent.

The substance is nearly insoluble in petroleum, ethyl acetate, chloroform, carbon disulphide, or water, but dissolves somewhat readily in methyl or ethyl alcohol; it separates slowly from an alcoholic solution in well-defined, glistening octahedra. When heated slowly, the semicarbazone contracts at  $140$ — $145^\circ$ , at a higher temperature it swells to an opaque mass, and at  $197^\circ$  is suddenly converted into a clear liquid which rapidly evolves gas, but without darkening in colour.

Crushed fragments of the octahedra, examined in cedar-wood oil by convergent, polarised light, show occasionally the acute bisectrix of a biaxial interference figure of moderate angle. The double refraction is strong and positive in sign.

The *oxime*,  $\text{CO}_2\text{H}\cdot\text{C}(\text{CH}_3)_2\cdot\text{CH}_2\cdot\text{C}(\text{CH}_3):\text{N}\cdot\text{OH}$ , was made by warming the acid in aqueous solution with hydroxylamine for a few minutes, and was isolated by rendering the solution faintly acid with hydrochloric acid and extracting with ether. The residue from the dried ethereal extract was triturated with a little dilute alcohol, and slowly became crystalline. After being dried on porous earthenware, it was crystallised from a mixture of ether and ethyl bromide.

0.1829 gave 0.3560  $\text{CO}_2$  and 0.1384  $\text{H}_2\text{O}$ .  $\text{C} = 53.1$ ;  $\text{H} = 8.4$ .

$\text{C}_7\text{H}_{13}\text{O}_3\text{N}$  requires  $\text{C} = 52.8$ ;  $\text{H} = 8.2$  per cent.

The oxime dissolves readily in methyl or ethyl alcohol, ethyl acetate, benzene, chloroform, or ether, somewhat readily in ethyl bromide, but is only sparingly soluble in boiling light petroleum, in which it fuses to a clear liquid. It separates on spontaneous evaporation of its solution in a mixture of ether and ethyl bromide as transparent, pyramidal crystals which melt at  $93$ — $94^\circ$ .

When crushed fragments of the crystals are examined in convergent polarised light, they show occasionally the acute bisectrix of a figure

of moderate angle. The double refraction is positive and strong. After melting between glass slips, the substance solidifies very slowly in numerous isolated, small, spindle-shaped plates.

The *phenylhydrazone*,  $\text{CO}_2\text{H}\cdot\text{C}(\text{CH}_3)_2\cdot\text{CH}_2\cdot\text{C}(\text{CH}_3):\text{N}_2\text{H}\cdot\text{C}_6\text{H}_5$ , was prepared by mixing cold dilute aqueous solutions of the acid and phenylhydrazine acetate; it separates rapidly in beautiful, white plates, and may be purified, when dry, by recrystallisation from benzene. On analysis of a specimen dried by exposure over sulphuric acid in a vacuum:

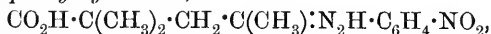
0.1547 gave 0.3782  $\text{CO}_2$  and 0.1045  $\text{H}_2\text{O}$ .  $\text{C} = 66.6$ ;  $\text{H} = 7.5$ .

$\text{C}_{13}\text{H}_{18}\text{O}_2\text{N}_2$  requires  $\text{C} = 66.6$ ;  $\text{H} = 7.7$  per cent.

The phenylhydrazone is somewhat readily soluble in ethyl acetate, ethyl or methyl alcohol, or in acetone, as well as in hot benzene or chloroform, but dissolves only sparingly in light petroleum; it separates from hot benzene or dilute alcohol in thin, colourless, pearly plates of considerable size, which melt at  $135^\circ$ . The crystals, which probably belong to the orthorhombic system, have straight extinction, and present the appearance of elongated, six-sided plates, and the acute bisectrix of the crystals emerges perpendicularly through the large faces; the double refraction is moderate and positive in sign. When fused on a glass slip beneath a cover glass, it solidifies on cooling, somewhat slowly, to masses of small plates, which are apparently identical in crystallographic character with the crystals from benzene or alcohol.

The phenylhydrazone dissolves in sodium carbonate solution, and is reprecipitated unaltered on acidifying with acetic acid. When exposed to the air and light, however, it rapidly becomes brown, and is finally converted into a dark brown resin.

The *p-nitrophenylhydrazone*,



is easily isolated from even very dilute solutions of the acid on adding the corresponding hydrazine acetate; it may be purified by crystallisation from ethyl acetate or glacial acetic acid.

0.1629 gave 0.3351  $\text{CO}_2$  and 0.0901  $\text{H}_2\text{O}$ .  $\text{C} = 56.1$ ;  $\text{H} = 6.1$ .

$\text{C}_{13}\text{H}_{17}\text{O}_4\text{N}_3$  requires  $\text{C} = 55.9$ ;  $\text{H} = 6.1$  per cent.

This substance dissolves readily in alcohol and in hot glacial acetic acid, and less readily in ethyl acetate, but is very sparingly soluble in light petroleum, benzene, or chloroform; it separates from hot ethyl acetate or glacial acetic acid in beautiful, six-sided plates, and in flat needles from dilute acetic acid. When heated slowly, it softens above  $180^\circ$ , and melts with effervescence at  $190^\circ$ .

The larger crystals are yellow, probably orthorhombic, plates, which

show slight dichroism, and have one direction of good cleavage. Crushed fragments, observed in convergent polarised light, occasionally show an axis of a wide-angled biaxial interference figure; the double refraction is very strong. When melted between glass slips, the substance solidifies very slowly when cold, but if kept warm the material crystallises more rapidly, but still incompletely, to a mixture of plates and needles with straight extinction, apparently identical in crystallographic character with the forms described above. Here and there the bisectrix of a crystal emerges perpendicularly to the field, and if, as is probably the case, this is the obtuse bisectrix, the double refraction is positive in sign; the axial dispersion is moderate.

*Action of Alkaline Sodium Hypobromite on Mesitonic Acid.*

*Formation of as-Dimethylsuccinic Acid,  $\text{CO}_2\text{H}\cdot\text{C}(\text{CH}_3)_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ .*

A solution containing 5 grams of mesitonic acid in 100 grams of dilute sodium hydroxide was warmed on the water-bath while a solution of bromine in 10 per cent. sodium hydroxide was added in small quantities, the end of the reaction being ascertained by removing a small portion of the solution 5 minutes after the last addition of hypobromite, and observing whether bromine was liberated on addition of strong hydrochloric acid. An excess of sodium sulphite was then added, the whole evaporated nearly to dryness, strongly acidified with hydrochloric acid, and extracted repeatedly with ether. The dried extracts after evaporation slowly crystallised on cooling, and the product was purified by draining on porous earthenware and crystallising from hot ethyl acetate.

0.1909 gave 0.3413  $\text{CO}_2$  and 0.1071  $\text{H}_2\text{O}$ .  $\text{C} = 49.2$ ;  $\text{H} = 6.7$ .

$\text{C}_6\text{H}_{10}\text{O}_4$  requires  $\text{C} = 49.3$ ;  $\text{H} = 6.9$  per cent.

0.2028 gram required 27.85 c.c. *N*/10 sodium hydroxide for neutralisation with phenolphthalein as indicator, making the equivalent of the acid 72.8, that is, practically identical with that required for a dibasic acid,  $\text{C}_{10}\text{H}_{10}\text{O}_4$ , namely, 73.

The identity of the acid with *as*-dimethylsuccinic acid was proved by a thorough examination of its general properties. It formed needles melting at  $140\text{--}141^\circ$ , and, when boiled with acetyl chloride, it was easily converted into a fusible anhydride. Finally, the anilic acid was prepared by the usual method, and found to consist of flat needles melting at  $185\text{--}186^\circ$ .

*Mesitononitrilecyanohydrin*,  $\text{CN} \cdot \text{C}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \text{C}(\text{CH}_3)(\text{OH}) \cdot \text{CN}$ .

In preparing the cyanohydrin of mesitylic nitrile, it was found unnecessary to isolate the intermediate product. The mixture, prepared by heating together 3.9 grams of mesityl oxide dissolved in 25 c.c. of alcohol and 5 grams of potassium cyanide (2 mols.) in 15 c.c. of water during 15 minutes on the water-bath, is cooled and carefully mixed with glacial acetic acid or dilute hydrochloric acid; the introduction of acid is best effected by means of a test-tube drawn out at its centre to a long capillary which reaches to the bottom of the liquid, and the whole is cooled during the operation by a stream of water.

As effectual treatment depends on the presence of the salt of hydrocyanic acid, care must be taken that the liquid remains alkaline, but only faintly so, during about an hour, when a distinct excess of acid is added, an operation which renders the cyanohydrin stable, and the solution is then diluted with an equal bulk of water, when alcohol for the most part is removed by evaporation on the water-bath.

The product is best isolated by saturating the liquid with ammonium sulphate and extracting repeatedly with chloroform. On removal of the latter, the extracted material becomes almost solid, and when drained in the usual way may be purified by recrystallisation from ethyl acetate.

0.1798 gave 26.6 c.c. at  $2350^\circ$  and 769 mm.  $N = 18.3$ .

$\text{C}_8\text{H}_{12}\text{ON}_2$  requires  $N = 18.4$  per cent.

The cyanohydrin is to some extent soluble in water, especially near the boiling point of the latter; it is much less readily soluble in solutions of inorganic salts, and is mostly precipitated from its cold aqueous solution on saturating the latter with ammonium sulphate in the form of nacreous plates or aggregates of flat needles. It is sparingly soluble in light petroleum, more readily so in ether or carbon disulphide, is freely dissolved by chloroform, and to a less marked extent by ethyl acetate. It separates from a mixture of ethyl acetate and light petroleum in slender, flattened needles, which melt sharply at  $165\text{--}166^\circ$ . The extinction directions of the crystals in polarised light are about  $20^\circ$  to their length, the double refraction being weak, and the elasticity in the direction of greatest length exceeds that at right angles to it. When melted on a glass slide below a cover-slip, the compound sets rapidly when cold to radiate masses of minute needles; if, however, the crystallisation of the material is started while the mass is cooling slowly, solidification occurs in well-defined, flat plates. The solidified material, when examined in convergent

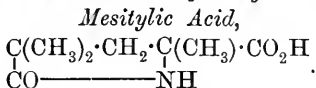
polarised light, shows occasionally the bisectrix of a wide-angled interference figure emergent normal to the field; in the probable event of this being the obtuse bisectrix, the double refraction of the crystals is negative in sign.

The cyanohydrin \* is distinctly acidic in character, being much more easily soluble in solution of sodium hydroxide than in water; from the resulting solution, it is reprecipitated on addition of an acid and even of sodium hydrogen carbonate.

The dissolution of the compound in cold sodium hydroxide does not appear to decompose it to any very marked extent; thus, if the solution is poured into excess of mineral acid, which would prevent recombination of the constituents, no odour of prussic acid can be detected; if, however, the alkaline solution is heated to boiling, cooled, and the foregoing experiment repeated, hydrocyanic acid was eliminated, and recognised by its odour and by other tests.

Strong mineral acids, such as cold saturated hydrochloric or hydrobromic acid, dissolve the substance without difficulty in the cold; this behaviour is, however, characteristic of nitriles, and is the result of the basic character of the cyano-group (compare J. Walker, *Ber.*, 1901, 34, 4117).

*Hydrolysis of Mesitononitrilecyanohydrin. Formation of*



This hydrolysis is easily accomplished by using cold saturated hydrochloric acid, in which case the action requires about 5 days, or more rapidly by warming the compound with ordinary hydrochloric acid on the water-bath for about 12 hours. On evaporation, the product separates in a crystalline form, and may be purified, after drying for some hours at 100°, by crystallisation from acetone. For analysis, the material was dried at 100°.

0.1633 gave 0.3376 CO<sub>2</sub> and 0.1123 H<sub>2</sub>O. C = 56.4; H = 7.6.

C<sub>8</sub>H<sub>13</sub>O<sub>3</sub>N requires C = 56.2; H = 7.6 per cent.

The compound was acidic in character, and had all the properties of mesitylic acid.

The crystals from acetone are anhydrous and present the appearance of short, rectangular prisms, quite unlike the hydrated needles which are obtained on crystallising the solution from water. An examination of crushed fragments of the crystals in cedar-wood oil by

\* An account of experiments on the acidity of this substance is given elsewhere (p. 1212).

convergent polarised light reveals the fact that the crystals are biaxial in character, the axial angle being moderately wide and with weak dispersion. The double refraction is positive in sign.

When melted between glass slips, the acid solidifies quickly, on cooling, in numerous opaque radiate patches.

The author desires to express his thanks to the Research Fund Committee of the Chemical Society for a grant which defrayed part of the cost of the investigation.

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### CXXIV.—*The Bromination of Phenols.*

By JOHN THEODORE HEWITT, JAMES KENNER, and HARRY SILK.

IN the interaction of bromine and phenol it is easy to prepare the 2:4:6-tribromo-derivative by using three molecular proportions of bromine. When, however, one or two molecular proportions of bromine are employed, mono- or di-bromo-derivatives may be made the chief products of reaction. Generally these substances as formed are also attacked by the bromine to a certain extent, with the result that the final product usually contains a certain amount of tribromophenol together with a small amount of the unsubstituted compound.

That the hydrobromic acid produced has an influence on the proportion of the products formed is fairly evident, and it seemed well worth while to examine the course of the reaction when the amount of mineral acid was increased, as well as when its action was eliminated by removing the free hydrobromic acid as quickly as produced by brominating in glacial acetic acid solution in presence of sodium acetate. The results to be obtained from such investigation are twofold; firstly, some insight may be obtained into the mechanism of the reaction, secondly, rational methods of procedure may be devised for obtaining the maximum yield of any desired substitution product.

Briefly, it may be said that the effect of adding concentrated sulphuric acid to a glacial acetic acid solution of phenol is to very largely retard the rate of bromination and to favour the entry of bromine into the para-position. The theoretical consideration of the results obtained will be discussed subsequently.

*Monobromination of Phenol, Sodium Acetate being present.*

Forty-seven grams of phenol and 50 grams of fused sodium acetate were dissolved in 250 c.c. of warm glacial acetic acid and the solution cooled, much of the sodium acetate separating with production of a pasty mass. Keeping this mixture well shaken and cooled below 25°, a solution of 80 grams of bromine in 100 c.c. of glacial acetic acid was gradually added. The bromine disappeared immediately, the mass was poured into water, neutralised with sodium carbonate, the oil removed, and the aqueous solution extracted with ether. The ethereal extract and the oil were united, dried with calcium chloride, and the ether removed by distillation; the residue of bromophenols weighed 76 grams. To determine the relative proportions of ortho- and para-bromophenols produced, the method devised by Meldola and Streatfeild (Trans., 1898, 73, 681) of nitrating the bromo-compounds and separating the bromonitrophenols produced was employed; we, however, modified the process of nitration in that 40.2 grams of the crude monobromophenols were dissolved in 50 c.c. of glacial acetic acid, and 11 c.c. of nitric acid (sp. gr. 1.5) in 50 c.c. of glacial acetic acid added gradually with cooling. After thirty minutes, 47.4 grams of acetic anhydride (rather over two molecular proportions) were also added, the whole allowed to stand eighteen hours, and then poured into water. The oil which separated solidified on standing; 36.5 grams of nitro-bromophenols were thus obtained. On separation by Meldola and Streatfeild's method of distillation in a current of steam, 19.8 grams of the volatile 4-bromo-2-nitrophenol were isolated, corresponding with about 55 per cent. of the crude nitration product.

*Monobromination of Phenol in Glacial Acetic Acid Solution.*

Using the same quantities of materials as in the last experiment, with the exception that no sodium acetate was added, and otherwise proceeding as before, we obtained 84 grams of crude bromophenols. Thirty-six grams of this mixture furnished 36 grams of mixed nitro-bromophenols, of which 23 grams of 2-nitro-4-bromophenol passed over in a current of steam. Of the amount of nitrobromophenols produced, 64 per cent. corresponded with the derivative of *p*-bromophenol.

*Monobromination of Phenol in presence of Sulphuric Acid.*

The same quantities of materials were again employed, except that the 250 c.c. of glacial acetic acid contained 75 grams of concentrated sulphuric acid as well as 47 grams of phenol. In two experiments,

83 grams and 70 grams respectively of mixed bromophenols were obtained, in the latter case some of the product having been accidentally upset. The total yield, taking the first experiment, is practically identical with that obtained without addition of sulphuric acid; the nitration experiment showed, however, that the proportion of bromine entering the para-position had been slightly increased. Forty grams of crude bromophenols furnished 34.5 grams of mixed nitro-derivatives, of which 24 grams were volatile in steam; this corresponds with about 70 per cent. of the nitrated bromo-phenols, consisting of the nitration derivative of *p*-bromophenol.

### *Dibromination of Phenol.*

If phenol be dissolved in a mixture of glacial acetic and concentrated sulphuric acids and treated with bromine, the first molecule is absorbed fairly rapidly; the velocity of reaction then falls off, and to introduce three atoms of bromine into the phenol molecule may take a week at the ordinary temperature in a solution to which concentrated sulphuric acid has been added. The extreme slowness with which the third bromine atom enters under such conditions allows 2:4-dibromophenol to be prepared conveniently in a state of purity. The acetic acid as solvent may, in fact, be dispensed with for the phenol and 73 per cent. sulphuric acid ( $\text{H}_2\text{SO}_4, 2\text{H}_2\text{O}$ ) used in its place.

Forty-seven grams of phenol were dissolved in a slightly warmed mixture of 100 grams of water and 300 grams of concentrated sulphuric acid (ordinary pure 98 per cent.  $\text{H}_2\text{SO}_4$ ). One hundred and sixty grams of bromine dissolved in 80 grams of glacial acetic acid were added with cooling and stirring, the bromine being rapidly used up under these conditions. The supernatant liquid was decanted, diluted, and filtered from any small amount of the dibromophenol. The residue was washed with water, and the remaining oil was found to solidify on sowing with a crystal of 2:4-dibromophenol. The weight of the dried crystalline cake was 117 grams, the yield being 93 per cent. of that theoretically obtainable. The melting point of the crude product was 26–30° and was raised by one recrystallisation from petroleum spirit or dry ether to 34–35°.\*

*p*-Bromophenyl benzoate,  $\text{C}_6\text{H}_5\cdot\text{CO}_2\cdot\text{C}_6\text{H}_4\text{Br}$ , as obtained by the Schotten-Baumann method from the product of the action of bromine

\* The melting point is given by Körner as 40° (*Annalen*, 1866, 137, 205); Peratoner, however, gives the melting point as 35–36° (*Gazzetta*, 1886, 16, 402). It is likely that Peratoner had the purer specimen, since he obtained it from 3:5-dibromosalicylic acid by heating with dilute sulphuric acid to 220–230°.

on phenol or from diazotised *p*-bromoaniline, separates from hot benzene as colourless crystals melting at 101—102°.

0.1180 gave 0.0805 AgBr. Br = 29.0.

$C_{13}H_9O_2Br$  requires Br = 28.9 per cent.

The ease with which this substance is produced in alkaline solution and its sparing solubility in cold benzene would probably furnish a ready method of isolating *p*-bromophenol from a mixture containing the ortho-isomeride and unattacked phenol.

#### *Bromination of Salicylic Acid.*

By adding sulphuric acid to an acetic acid solution of salicylic acid, the entry of bromine into the molecule can be much delayed. This is especially the case with the second atom of the substituting element, position 3 in the salicylic acid molecule ( $CO_2H : OH = 1 : 2$ ) being attacked very slowly. If salicylic acid (1.38 grams) dissolved in glacial acetic acid (15 c.c.) and strong sulphuric acid (4 grams) be treated with two molecules of bromine (3.2 grams in acetic acid solution), even after five days, a considerable amount of bromine is still to be found in the free condition. Use can be made of this result in the preparation of 5-bromosalicylic acid.

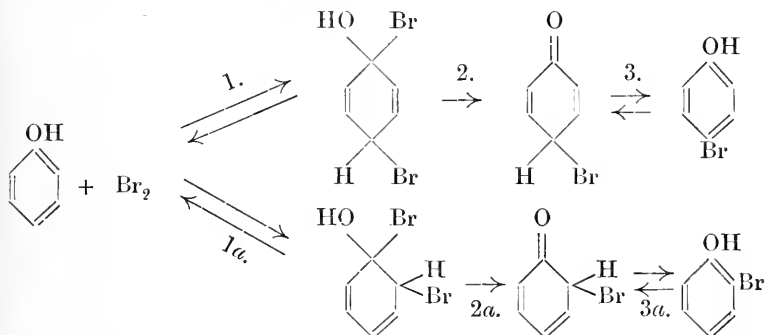
13.8 grams of salicylic acid were dissolved in 100 c.c. of glacial acetic acid and 20 grams of pure sulphuric acid added; 50 c.c. of a solution of bromine (16 grams) in glacial acetic acid were run in at a temperature of 30—40°. The mixture was then gently warmed for 30 minutes under reflux, and the acetic acid subsequently removed by distillation under diminished pressure (temperature 50°). The remaining liquid deposited 17.5 grams of crystals on cooling, which, after collection, washing, and drying, melted at 161—163°. Hübner and Heinzerling (*Zeit. für Chem.*, 1871, 709) give the melting point of 5-bromosalicylic acid as 164—165°, hence about 80 per cent. of a practically pure product was obtained. A further 1.8 grams (about 8 per cent.) were recovered by diluting the mother liquor; this, however, softened at 147° and melted at about 150°.

#### *Bromination of $\alpha$ -Naphthol.*

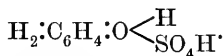
We hoped to be able to influence the bromination of  $\alpha$ -naphthol in the same way and so obtain 4-bromo- $\alpha$ -naphthol. In this we were disappointed; by using one molecular proportion of bromine in presence of glacial acetic and concentrated sulphuric acids, 2:4-dibromonaphthol and unchanged  $\alpha$ -naphthol were recovered.

*Discussion of the Results.*

It will be noted immediately that our result in the case of phenols is apparently the direct opposite of that obtained by Lapworth in the case of acetone and bromine in dilute aqueous solution (Trans., 1904, 85, 30). Lapworth, finding that the bromination of acetone was accelerated by hydrogen ions, supposes that these convert ketonic acetone into the enolic form. The present authors think that it is hydroxylic phenol which yields substitution derivatives, but suppose that strong acids in absence of water transform phenol into a keto-dihydrobenzene (*cyclohexadienone*), or rather into an oxonium salt thereof. The relationship between phenol and bromine may perhaps be represented in the following manner : \*



Now the reversible changes 1 and 1a have greater velocities than the irreversible changes 2 and 2a. If the change 2 can be relatively accelerated more than the change 2a, or the retardation of reaction be greater in the case of 2a than of 2, the yield of the para-derivative will ultimately be increased, whilst that of the ortho-compound is correspondingly diminished. The authors think that the sulphuric acid favours the ketonic modification owing to the formation of salts of the oxonium type,

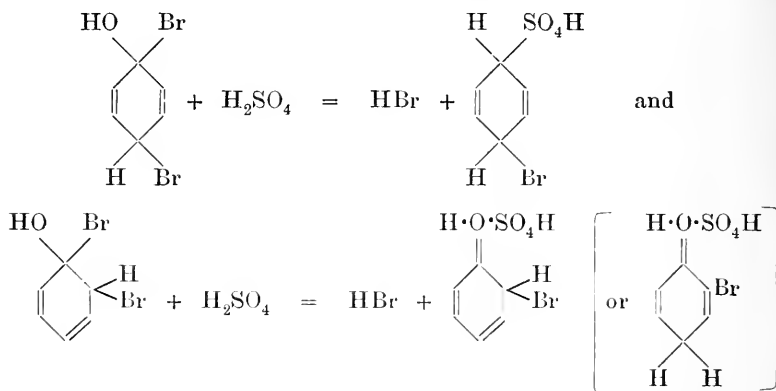


Following the analogy of the bromoanilines, *p*-bromophenol, although an extremely weak base, would be more readily capable of producing

\* For an account of the mechanism of substitution, especially in the aromatic series, reference may be made to Armstrong (Trans., 1887, 51, 258; Proc., 1896, 12, 230; 1899, 15, 176), Armstrong and Davis (Proc., 1896, 12, 230), Lapworth (Trans., 1898, 73, 445), and Thiele (*Annalen*, 1899, 306, 125—136).

Respecting bromo-derivatives of *cyclohexadienone*, see Auwers (*Ber.*, 1895, 28, 2888; 1896, 29, 1095), and various other papers; also Zincke (*Ber.*, 1895, 28, 3121).

oxonium salts of the type mentioned than *o*-bromophenol, hence of the two reactions represented by the equations:



the former should take place far more readily than the latter, and the production of *p*-bromophenol be favoured at the expense of the isomeric ortho-compound.

A similar explanation holds in the case of salicylic acid; it is, however, remarkable that such a wide divergence should be observed in the naphthalene series. Once more one notices the essential difference in structure between benzene and naphthalene derivatives.

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### CXXV.—6-*Aminocoumarin*.

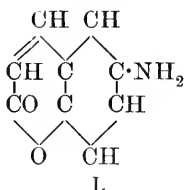
By GILBERT THOMAS MORGAN and FRANCES MARY GORE MICKLETHWAIT.

THE greater reactivity towards diazonium compounds exhibited by the amines of the naphthalene series when compared with the benzenoid bases is intimately connected with the existence in their molecules of two unsaturated cyclic systems, for when the unsubstituted ring is completely hydrogenated, the tetrahydronaphthalene bases thus produced are found to be endowed with the properties of the amines of the benzene series.

Tetrahydro- $\beta$ -naphthylamine, in its interaction with nitrous acid or diazonium salts, behaves as an analogue of *p*-toluidine (C. Smith, Trans., 1902, 81, 900), and although tetrahydro- $\alpha$ -naphthylamine still retains the naphthalenoid character of yielding azo-derivatives without the intermediate formation of diazo-amines (Bamberger and Bordt,

*Ber.*, 1889, 22, 625), yet its para-substituted derivatives behave in this respect exactly like the corresponding compounds of aniline (Morgan, Micklethwait, and Winfield, this vol., p. 739).

Comparative experiments have now been made on 6-aminocoumarin \*



(Frapolli and Chiozza, *Annalen*, 1855, 95, 252) with the view of ascertaining whether the presence of the unsaturated lactonic ring would, as in the case of the unsaturated hydrocarbon ring in the naphthalene compounds, bring about any increase in the reactivity of the amine towards diazonium salts.

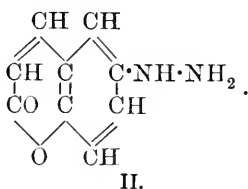
6-Aminocoumarin, when treated with nitrous acid, yields a very sparingly soluble compound which undergoes fission on treatment with concentrated mineral acids into a mixture of the salts of the original base and its diazonium compound. Diazonium salts, such as *p*-nitrobenzenediazonium chloride, furnish similar diazo-amines, and hence the base behaves in this respect like any other para-substituted benzenoid amine, the presence of the lactonic ring having no apparent influence on the course of the foregoing changes.

In carrying out these experiments, the singular colour of 6-aminocoumarin and its derivatives attracted attention, and the investigation was extended in order to ascertain whether any connection could be traced between the colour of these coumarin derivatives and their chemical nature.

Although derived from coumarin, a colourless lactone, 6-aminocoumarin, is a bright yellow compound and retains its colour after repeated crystallisations. Its salts with the mineral acids are, however, colourless, and so are its acyl derivatives containing formyl, acetyl, lactyl, benzoyl, and benzenesulphonyl groups. The quaternary methobromide and methiodide, obtained by completely methylating the base, are likewise devoid of colour, as are also its diazonium salts, the acyl derivatives, and salts of its hydrazine and monoalkylated derivatives, the nitrosoamines of the latter bases, and the salts of the tertiary base, dimethyl-6-aminocoumarin.

\* The constitution of this base follows from the synthesis of 6-nitrocoumarin from 5-nitrosalicylaldehyde and the oxidation of the nitro-compound to 5-nitrosalicylic acid (Tagee, *Ber.*, 1887, 20, 2109), additional evidence being furnished by the synthesis of 6-aminocoumarin itself by the electrolytic reduction of *m*-nitrocinnamic acid (Gattermann, *Ber.*, 1894, 27, 1937).

On the other hand, the mono- and di-alkylated 6-aminocoumarins are distinctly coloured like the parent substance, and 6-*coumarylhydrazine*,



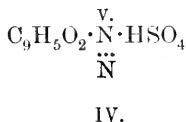
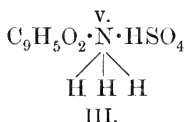
obtained by the partial reduction of the colourless diazonium salts, is also distinctly yellow.

*Benzylidene-6-aminocoumarin* occupies an intermediate position between the free base and its acyl derivatives, for, although it is distinctly coloured, the shade of yellow is much paler than that of the original base.

In short, all the bases of this series are coloured, whilst their salts and acyl derivatives are colourless. The appearance of colour in this group of substances seems to depend on the presence in the molecule of the free basic radicles,  $\text{NH}_2$ ,  $\text{NHR}$ , or  $\text{NR}_2$ , for when the basic character of these groups is destroyed by the substitution of one hydrogen by an acyl radicle or by the formation of a salt, then the colour disappears. As, however, the amino-derivatives of benzene are in general colourless substances, the development of colour in this particular case is probably due to some mutual interaction of the amino-group and the unsaturated coumarin residue. It is hardly likely that the group  $\text{CH}:\text{CH}$  in the latter complex participates in the production of this effect, otherwise it might be expected that the naphthylamines would be coloured owing to the presence in their molecules of an unsaturated ring containing, at least potentially, two of these ethylenic groups. It is probably the residue  $-\text{CO}\cdot\text{O}-$  acting in conjunction with the amino-group which brings about this appearance of colour.

The lactonic oxygen is in the para-position with respect to the amino-group, and, with this orientation, the unsaturated groups  $-\text{O}\cdot\text{CO}-$  and  $\text{NH}_2$  ( $\text{NHR}$  or  $\text{NR}_2$ ) are especially likely to exercise some action on each other in virtue of their residual affinities, but although these considerations suggest a probable rearrangement of the valencies in the molecule of the compound, the exact nature of this alteration can scarcely be rigidly formulated until further experimental data are available. The colour effect in the case of the 6-aminocoumarin can, however, scarcely be due to any migration of its aminic hydrogen atoms, inasmuch as these phenomena are not appreciably modified by the replacement of both hydrogens by alkyl groups, as in the case of *dimethyl-6-aminocoumarin*.

In this connection, the colour relationship of the diazo-derivatives is of interest. According to the prevailing view, a diazonium salt is regarded as containing pentadic nitrogen as in formula IV, and the fact that colourless 6-aminocoumarin sulphate gives rise to a colourless diazonium salt supports the hypothesis that the two compounds have a similar configuration :



On the contrary, the unstable diazocyanide derived from the latter substance is yellow, and probably contains only trivalent nitrogen.

#### EXPERIMENTAL.

Coumarin (100 grams) was dissolved in 120 c.c. of glacial acetic acid and treated with a mixture of 56 c.c. of nitric acid of sp. gr. 1.5 and 40 c.c. of glacial acetic acid ; no appreciable rise of temperature was observed, but, on adding 100 c.c. of concentrated sulphuric acid, a vigorous reaction took place ; the mixture was therefore cooled at first, and finally heated for a short time on the water-bath. A portion of the nitrocoumarin crystallised, and the remainder was precipitated by pouring the acid mother liquor into ice-water. The first product, when recrystallised from benzene, separates as a mass of white, prismatic crystals melting at 181—182° ; Taege, *loc. cit.*, gives 185°.

The nitro-compound (2 parts) was suspended in 50 parts of hot water acidified with 1 part of concentrated hydrochloric acid, and reduced by the gradual addition of 4 parts of iron filings ; the mixture was finally heated on the sand-bath, rendered alkaline with sodium hydrogen carbonate, and rapidly filtered at the pump. The filtrate, on cooling, yielded 1.2—1.4 parts of 6-aminocoumarin, which separated from the solution in long, yellow needles. A portion of the base was crystallised once from alcohol, and then thrice from benzene ; it then had the form of clear, straw-yellow needles melting at 163—164°. Frapelli and Chiozza give the melting point as 168—170°, whilst Taege and Gattermann found it to be 161° and 168° respectively.

The salts of 6-aminocoumarin are well-defined, crystalline, colourless substances soluble in water, the hydrochloride dissolves only sparingly in alcohol, whilst the sulphate may be precipitated in colourless crystals from glacial acetic acid.

*Formyl-6-aminocoumarin*,  $\text{C}_9\text{H}_5\text{O}_2 \cdot \text{NH} \cdot \text{COH}$ , prepared in the usual

way, crystallised from water in colourless crystals melting at  $175-176^{\circ}$ :  $N = 7.59$ ;  $C_{10}H_7O_3N$  requires  $N = 7.40$  per cent.

*Lactyl-6-aminocoumarin*,  $C_9H_5O_2 \cdot NH \cdot CO \cdot CH(OH) \cdot CH_3$ , gradually separated on warming a saturated solution of the base in lactic acid; the precipitation was completed by diluting the mixture with aqueous ammonia; the substance, when recrystallised from hot water, separated as a felted mass of colourless, silky needles melting at  $159-160^{\circ}$ :  $N = 5.95$ ;  $C_{12}H_{11}O_4N$  requires  $N = 6.00$  per cent.

*Benzenesulphonyl-6-aminocoumarin*,  $C_9H_5O_2 \cdot NH \cdot SO_2 \cdot C_6H_5$ , was prepared from the base and benzenesulphonic chloride by the Schotten-Baumann method, using sodium carbonate instead of sodium hydroxide; it crystallises from water or benzene in colourless crystals melting at  $159^{\circ}$ :  $N = 4.02$ ;  $C_{15}H_{11}O_4NS$  requires  $N = 4.38$  per cent.

The foregoing acyl derivatives and the acetyl and benzoyl compounds described by Gattermann (*loc. cit.*) are all colourless substances.

*Benzylidene-6-aminocoumarin*,  $C_9H_5O_2 \cdot N : CH \cdot C_6H_5$ , produced by the condensation of its generators in glacial acetic acid solution, crystallised from benzene in pale yellow, flattened needles melting at  $150-152^{\circ}$ :  $C = 77.18$ ;  $H = 4.11$ ;  $C_{16}H_{11}O_2N$  requires  $C = 77.11$ ;  $H = 4.41$  per cent.

## I. The Diazo-reactions of 6-Aminocoumarin.

### 1. Action of Diazo-compounds on 6-Aminocoumarin.

*6:6'-Diazaminocoumarin*,  $C_9H_5O_2 \cdot N_2 \cdot NH \cdot C_9H_5O_2$ , produced by diazotising 1 molecular proportion of 6-aminocoumarin and adding the solution to an equal amount of the base dissolved in alcohol, separated at once as a brownish-yellow precipitate (m. p.  $230-234^{\circ}$ ), which was too sparingly soluble in the ordinary organic solvents to admit of recrystallisation:  $N = 12.47$ ;  $C_{18}H_{11}O_4N_3$  requires  $N = 12.61$  per cent. The diazo-amine dissolved in alcoholic potash to a green solution, and, when treated with cold concentrated solutions of the mineral acids, underwent the characteristic fission of a diazo-amine, yielding 6-aminocoumarin and the corresponding diazonium base; the solution, when diluted and filtered into an alkaline solution of  $\beta$ -naphthol, gave *coumarin-6-azo- $\beta$ -naphthol*,  $C_9H_5O_2 \cdot N_2 \cdot C_{10}H_6 \cdot OH$ , a substance which was also produced by the direct action of diazotised coumarin on the  $\beta$ -naphthol. This azo-compound, unlike the azo- $\beta$ -naphthols derived from aniline and its homologues, is somewhat soluble in aqueous alkali hydroxides; it crystallises from glacial acetic acid in well-defined, brownish-red needles melting at  $222^{\circ}$ :  $C = 72.83$ ;  $H = 3.91$ ;  $N = 8.59$ ;  $C_{19}H_{12}O_3N$  requires  $C = 72.15$ ;  $H = 3.80$ ;  $N = 8.86$  per cent.

*p-Nitrobenzenediazo-6-aminocoumarin*,  $NO_2 \cdot C_6H_4 \cdot N_2 \cdot NH \cdot C_9H_5O_2$ , prepared from *p*-nitrobenzenediazonium chloride and 6-aminocoumarin

in alcoholic solution, is very sparingly soluble in the ordinary organic media: a small portion dissolved in ethyl acetate or acetone separated in yellow crystals, which decomposed violently at  $218-225^{\circ}$  when slowly heated, but remained unchanged until  $230^{\circ}$  when immersed in the warm melting point bath:  $N = 17.38$ ;  $C_{15}H_{10}O_4N_4$  requires 18.06 per cent. With alcoholic potash, this substance gives the magenta coloration characteristic of all diazo-amines derived from *p*-nitroaniline, but, on warming, the solution assumes a deep bluish-purple colour. This unsymmetrical diazo-amine, when decomposed by cold concentrated acid and poured on to ice, yielded a solution containing the diazonium salts of *p*-nitroaniline and 6-aminocoumarin; these substances, when coupled with  $\beta$ -naphthol in aqueous sodium hydroxide, gave rise to two azo-compounds, coumarin-6-azo- $\beta$ -naphthol, which remained dissolved in the alkali hydroxide, and *p*-nitrobenzeneazo- $\beta$ -naphthol, which was precipitated; the latter was crystallised from ethyl acetate and identified by its melting point ( $249^{\circ}$ ).

## 2. Diazo-derivatives of 6-Aminocoumarin.

The diazonium salts of 6-aminocoumarin are readily prepared by the ordinary process of diazotisation, and are fairly stable compounds yielding colourless solutions in water, alcohol, or glacial acetic acid. The authors have already employed solutions of the diazonium chloride in a comparative study of the action of diazo-compounds on the amines of the naphthalene and tetrahydronaphthalene series (this vol., pp. 750, 751).

*Coumarin-6-diazonium sulphate*,  $C_9H_5 \cdot O_2 \cdot N_2 \cdot HSO_4$ , was isolated in the solid form by dissolving 6-aminocoumarin in glacial acetic acid, precipitating the sulphate by the addition of 1 molecular proportion of concentrated sulphuric acid, and adding to the cooled mixture an excess of amyl nitrite, stirring vigorously until the insoluble sulphate had redissolved, and pouring the filtered solution into a mixture of ether and alcohol. The diazonium sulphate separated in colourless crystals, which became brown on exposure to the atmosphere; it was washed with ether and light petroleum and dried on a porous tile:  $S = 12.04$ ;  $C_9H_6O_6N_2S$  requires  $S = 11.85$  per cent. The diazonium salt underwent no further change on keeping, and after several days retained the property of coupling with  $\beta$ -naphthol-3:6-disulphonic acid ("R salt") in alkaline solution; it may therefore be regarded as an exceptionally stable example of its class.

*Coumarin diazocyanides*.—The preceding compound was extremely soluble in cold water, and its solution, when treated with aqueous potassium cyanide, yielded a voluminous, bright yellow precipitate

which rapidly assumed a green tinge before it could be separated from the mother liquor. Neither the yellow substance nor the green product formed an azo-compound with  $\beta$ -naphthol or "R salt."

### 3. 6-Coumarylhydrazine, $C_9H_5O_2 \cdot NH \cdot NH_2$ .

This primary hydrazine was obtained by diazotising 6-aminocoumarin (1 part) in cold concentrated hydrochloric acid with 20 per cent. aqueous sodium nitrite, and treating the product with excess of stannous chloride (4 parts) dissolved in 6 parts of concentrated hydrochloric acid diluted with an equal volume of water. A precipitate, which formed at first, redissolved, but after 12 hours the solution again became turbid; the precipitate was collected and cautiously treated with a saturated solution of sodium carbonate until it just gave an alkaline reaction with turmeric paper; the yellow product was then drained at the pump, the total yield being about 3.5 grams from 12 grams of the 6-aminocoumarin. The hydrazine crystallises from benzene, water, or the alcohols in canary-yellow needles melting at  $165-167^\circ$ , but the hydroxylic solvents seem to decompose it slightly; it is therefore preferably purified from benzene, the crystallisation being accelerated by the addition of light petroleum:  $C = 61.92$ ;  $H = 4.98$ ;  $N = 16.18$ ;  $C_9H_5O_2N_2$  requires  $C = 61.36$ ;  $H = 4.55$ ;  $N = 15.90$  per cent. The substance has the properties of a primary aromatic hydrazine; it readily reduces Fehling's solution, even in the cold, and when boiled with aqueous copper sulphate it loses the hydrazino-radicle and regenerates coumarin. The latter result is of interest, because it indicates that the unsaturated lactonic ring has not been affected by the changes involved in preparing this hydrazine from coumarin.

With pyruvic acid, the hydrazine gives a sparingly soluble, yellow hydrazone: the *benzylidene* compound,  $C_9H_5O_2 \cdot NH \cdot N : CH \cdot C_6H_5$ , separates from a glacial acetic acid solution of its generators, its formation being attended by an appreciable rise of temperature; it crystallises from benzene in aggregates of bright yellow needles melting indefinitely at  $190-194^\circ$ . When suspended in water and treated in the cold with acetic anhydride, the hydrazine yielded a colourless acetyl derivative melting at  $163^\circ$ :  $N = 12.44$ ;  $C_{11}H_{10}O_3N$  requires  $N = 12.84$  per cent. Repeated crystallisation of this acetylated compound seems to decompose it, a yellow solution being obtained having the odour of coumarin. The aqueous solution of the hydrazine salts of the mineral acids are also colourless.

II. *Alkylated 6-Aminocoumarins.*

6-Coumaryltrimethylammonium bromide,  $C_9H_5O_2 \cdot N(CH_3)_3Br$ , was obtained in brown needles when 6-aminocoumarin hydrobromide was heated with excess of methyl alcohol in sealed tubes at  $160^\circ$ . After removal of the methyl alcohol on the water-bath, the crystalline residue was crystallised either from water, in which it was readily soluble, or from absolute alcohol, in which it dissolved only sparingly. The quaternary bromide separated from the latter solvent in colourless needles melting at  $229^\circ$ :  $Br = 27.97$ ;  $C_{12}H_{14}O_2NBr$  requires 28.16 per cent.

6-Coumaryltrimethylammonium iodide,  $C_9H_5O_2 \cdot N(CH_3)_3I$ , was prepared by heating for half an hour in a reflux apparatus 6-aminocoumarin (1 mol.), methyl iodide (3 mols.), and potassium hydroxide (2 mols.); all dissolved in alcohol, the iodide being added gradually. The deposit obtained when crystallised from absolute alcohol separated in colourless needles melting and decomposing somewhat indefinitely at  $202\text{--}207^\circ$ :  $N = 4.43$ ;  $I = 38.18$ ;  $C_{12}H_{14}O_2NI$  requires  $N = 4.23$ ;  $I = 38.27$  per cent.

Dimethyl-6-aminocoumarin,  $C_9H_5O_2 \cdot N(CH_3)_2$ , was obtained from the quaternary bromide by treating the latter with precipitated silver oxide, evaporating the filtered solution on the water-bath, and finally heating at  $130^\circ$  for 3 hours. When cooled, the product became semi-crystalline, and on extraction with light petroleum yielded a small amount of orange-yellow, flattened needles, sometimes of considerable length; the base melts at  $85\text{--}86^\circ$ :  $C = 69.42$ ;  $H = 5.77$ ;  $C_{11}H_{11}O_2N$  requires  $C = 69.84$ ;  $H = 5.82$  per cent.

A slightly better yield of dimethyl-6-aminocoumarin was obtained by heating the methobromide at  $120^\circ$  and then adding a small amount of water; a vigorous evolution of gas takes place; the liquid product which became solid on cooling furnished the tertiary base on extraction with light petroleum (b. p.  $60\text{--}80^\circ$ ). When heated with an alcoholic solution of methyl iodide, dimethyl-6-aminocoumarin gave rise to the foregoing quaternary iodide (m. p.  $202\text{--}207^\circ$ ).

*Monoalkylated 6-Aminocoumarins.*

The secondary methyl and ethyl bases were prepared by heating benzenesulphonyl-6-aminocoumarin (p. 1234) in alcoholic solution with molecular proportions of potassium hydroxide and the appropriate alkyl iodide, and hydrolysing the alkylated sulphonamide thus produced with concentrated hydrochloric acid in sealed tubes at  $150\text{--}170^\circ$ , the heating in each step of this preparation being continued for about 3 hours.

*Benzenesulphonylethyl-6-aminocoumarin*,  $C_9H_5O_2 \cdot N(C_2H_5) \cdot SO_2 \cdot C_6H_5$ , was prepared in the manner indicated and isolated by distilling off the alcohol and diluting the residual solution with water; when crystallised from a mixture of benzene and light petroleum, it separated in colourless prisms melting at  $124^\circ$ .

*Ethyl-6-aminocoumarin*,  $C_9H_5O_2 \cdot NH \cdot C_2H_5$ , was obtained by hydrolysing the preceding compound with 4 parts of concentrated hydrochloric acid and neutralising the product with ammonia; it crystallised from light petroleum in yellow leaflets or flattened needles melting at  $83^\circ$ : C=70.11; H=5.89; N=7.77;  $C_{11}H_{11}O_2N$  requires C=69.84; H=5.82; N=7.40 per cent.

*6-Coumarylethylnitrosoamine*,  $C_9H_5O_2 \cdot N(C_2H_5) \cdot NO$ , separated as an oil, which rapidly changed to a pale brown solid, on treating the acid solution of the preceding base with sodium nitrite (1 mol.); it crystallised from light petroleum ( $80-100^\circ$ ) in well-defined, colourless needles (m. p.  $90^\circ$ ) which became brown on exposure to air: N=12.71;  $C_{11}H_{10}O_3N_2$  requires N=12.84 per cent. When dissolved in cold concentrated sulphuric acid containing a trace of phenol, the nitrosoamine developed a blue coloration.

*Benzenesulphonylmethyl-6-aminocoumarin*,  $C_9H_5O_2 \cdot N(CH_3) \cdot SO_2 \cdot C_6H_5$ , prepared exactly like its ethyl homologue, crystallised in short, colourless, refractive prisms and melted at  $165-167^\circ$ .

*Methyl-6-aminocoumarin*,  $C_9H_5O_2 \cdot NH \cdot CH_3$ , obtained in the manner previously described, crystallised from light petroleum (b. p.  $80-100^\circ$ ) in yellow needles melting at  $105-106^\circ$ : N=8.61;  $C_{10}H_9O_2N$  requires N=8.00 per cent.

*6-Coumarylmethylnitrosoamine*,  $C_9H_5O_2 \cdot N(CH_3) \cdot NO$ , crystallised from a mixture of benzene and light petroleum in well-defined, colourless needles melting at  $168-169^\circ$ , and was only very sparingly soluble in light petroleum; it gave intense colorations in all the phases of Liebermann's reaction.

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## CXXVI.—*The Resin Acids of the Coniferæ. Part I.* *The Constitution of Abietic Acid.*

By THOMAS HILL EASTERFIELD and GEORGE BAGLEY.

IN the vegetable as in the animal kingdom, the performance of similar physiological functions is in general correlated with a similarity in chemical products. Thus typical constitutions are

characteristic of several classes of vegetable substances such as the sugars and fixed oils, the general properties of which were familiar long before their chemistry was understood.

Analogy would seem to indicate that the vegetable resins, which are regarded by physiologists as waste products of plant metabolism, should have some common basis of constitution, or that at least a similar constitution should mark the resin acids derived from plants belonging to a common genus or even to a common order. With this idea as a working hypothesis, and as an introduction to the investigation of the numerous New Zealand *Coniferæ*, the authors have during the last four years sought to arrive at a constitutional formula for abietic acid.

At first sight it may appear as though the similarities between the resin acids are so few as scarcely to justify the search for a common basis of constitution. The following properties, however, appear to be common to those acids which have been carefully investigated :

1. They show in a marked degree the phenomenon of superfusion ; if quickly cooled, they set to a glass or resin having no definite melting point. This appears to be the most characteristic physical property of a resin.

2. They behave as unsaturated compounds of carbocyclic character, absorbing oxygen from the air, particularly when in a fused condition, and yielding nitro-derivatives if treated with nitric acid in cold glacial acetic acid solution.

3. They do not form esters when treated with alcohol and hydrochloric acid, and hence probably contain substituents in both ortho-positions with respect to their carboxyl group.

4. When treated with hydriodic acid, they readily yield hydrocarbons which have been generally regarded as diterpenes, although the proof of their terpenoid character is wanting.

In the case of abietic acid, the hydrocarbon resulting from the action of hydriodic acid is in reality produced by the elimination, not the reduction, of the carboxyl group, and this will probably be found to be the case with the hydrocarbons which Vesterberg (*Ber.*, 1886, 19, 2174) and Henry (*Trans.*, 1901, 79, 1155) obtained by the interaction of hydriodic acid and pimaric acid from different sources.

The hydrocarbon resulting from the action of hydriodic acid on abietic acid agrees in its physical properties with that obtained by the distillation of crystalline abietic acid and also by the distillation of American colophony. There can be little doubt that it is identical with the "colophene" which Deville (*Annalen*, 1841, 37, 193) isolated from the products of distillation of colophony, but its properties differ from those of the "colophene" which, according to the same author, results if turpentine is polymerised by sulphuric acid (*loc. cit.*, and

Henry, *Trans.*, 1901, **79**, 1156). The name *abietene* is adopted for the hydrocarbon from abietic acid, since in recent years the term colophene has generally been applied to the condensation product from turpentine.

Abietene,  $C_{18}H_{26}$ , agrees in specific gravity and refractive index with the "diterebenthyl" ( $C_{20}H_{30}$ ) of Renard (*Compt. rend.*, 1887, **105**, 865). Again, it is probably identical with the compound which Krämer and Spilker (*Ber.*, 1899, **32**, 2952) obtained by distilling colophony under pressure, and which Krämer (*Ber.*, 1899, **32**, 3614) regarded as being derived from abietic acid by the loss of carbon monoxide and dioxide. Krämer's analyses and molecular weight determinations agree with the formula  $C_{18}H_{26}$ , but he admits that the substance was of doubtful purity, and gives no physical constants with the exception of the boiling point ( $330-350^{\circ}$ ) (*Ber.*, 1900, **33**, 2267).

That resin oil is intimately related to retene was first shown by Kelbe (*Abstr.*, 1888, 605) who obtained retene by distilling resin oil with sulphur. The retene was supposed to be derived from tetrahydroretene in the resin oil (*Ber.*, 1888, **21**, Ref. 555). Bamberger and Strasser (*Ber.*, 1889, **22**, 3368) have pointed out that hydrogenated retenes are, in all probability, normal constituents of resin oil, whilst Krämer (*Ber.*, 1903, **36**, 647) states that resin oil is a hydrogenated retene. If Krämer's view is correct, abietic acid is probably a decahydroretenecarboxylic acid, a conclusion which the authors had deduced before their attention was drawn to his work on the subject.

The main object of the present paper is to show that abietic acid really has the constitution above mentioned; this is done by demonstrating that abietic acid is abietenecarboxylic acid, and that abietene is decahydroretene.

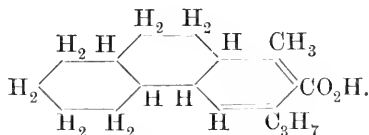
That abietic acid is abietenecarboxylic acid follows from the fact that when abietene is obtained from this acid by the action of hydriodic acid at  $200^{\circ}$ , the gases produced consist, to the extent of 90 per cent., of oxides of carbon, and that the volume of these gases corresponds approximately with that required for the elimination of a carboxyl group from abietic acid.

That abietene is decahydroretene is rendered highly probable from the observation that carefully purified abietene yields retene if distilled with sulphur, and, further, that abietene, when reduced at  $240^{\circ}$  with hydriodic acid and phosphorus, is almost entirely changed into a highly fluorescent hydrocarbon having the same composition and almost the same boiling point as the dodecahydroretene obtained by Liebermann and Spiegel (*Ber.*, 1889, **22**, 780) as the ultimate product of the reduction of retene with the same reagents. In this connection it is noteworthy that of the various polycyclic hydrocarbons reduced

by these authors, retene was the only one which failed to yield a perhydride.

Objection may be raised to the view that abietic acid is a hydrogenated retene-carboxylic acid on the ground that the accepted constitution for retene does not allow of the possibility of a diortho-substituted carboxylic acid. Bamberger and Hooker (*Ber.*, 1885, 18, 1755), however, to whom our knowledge of the constitution of retene is due, specifically state that in retene the methyl and isopropyl groups are merely assumed to be in the para-position with respect to one another.

That the alkyl groups in abietic acid, and hence also in retene, are really in the meta-position is rendered almost certain by the interesting observation of Kelbe (*Ber.*, 1884, 17, 1157) that resin spirit is rich in *m*-cymene. If the meta-position be accepted for these groups, the appended constitution will account for the chemical behaviour of abietic acid.



In particular, this formula accounts for :

1. The relationship of abietic acid to abietene, retene, and fichtelite.
2. The occurrence of *m*-cymene amongst the products of distillation.
3. The occurrence of trimellitic and isophthalic acids amongst the products of oxidation (Schreder, *Annalen*, 1874, 172, 94).
4. The optical activity, which does not disappear when the carboxyl group is eliminated.
5. The low velocity of esterification.

The question now arises whether any other resin acids from the *Coniferæ* are to be regarded as phenanthrene derivatives. It can hardly be doubted that pimaric acid is the next higher homologue of abietic acid, with which it is frequently associated in nature and from which it is separated with difficulty.

Again, podocarpic acid, investigated by Oudemans, yielded on distillation a crystalline hydrocarbon, "methanthrene," which has generally been regarded as a methylanthracene. The low melting point of the hydrocarbon (115°) and the yellow colour of the picric acid compound accord more satisfactorily with the assumption that methanthrene is a methylphenanthrene.

Rimuic acid, again (Easterfield and Aston, *Proc.*, 1903, 19, 190), is certainly a lower homologue of podocarpic acid, for the acids agree closely in their remarkable chemical behaviour.

The following constitutions thus become probable :

Rimuic acid,  $C_{16}H_{20}O_3$ , = oxymethylphenanthrenecarboxylic acid +  $4H_2$ .

Podocarpic acid,  $C_{17}H_{22}O_3$ , = oxydimethylphenanthrenecarboxylic acid +  $4H_2$ .

Abietic acid,  $C_{19}H_{28}O_2$ , = methylisopropylphenanthrenecarboxylic acid +  $5H_2$ .

Pimaric acid,  $C_{20}H_{30}O_2$ , = dimethylisopropylphenanthrenecarboxylic acid +  $5H_2$ .

Several points of minor interest have arisen during the progress of the present investigation, and of these the following may be mentioned:

When colophony is distilled under reduced pressure, it does not yield isosylvic anhydride, as stated by Bischoff and Nastvogel (*Ber.*, 1890, 23, 1921). The distillate has the composition of abietic (sylvic) acid, and when crystallised from alcohol yields ordinary abietic acid melting at  $160-165^\circ$ .

The distillation of colophony in superheated steam yields the same products as the distillation under reduced pressure. If the process is carried out on a manufacturing scale in a stearin still, the resin acids chiefly condense in the first two coils, whereas the more volatile abietene, together with decomposition products, is chiefly found in the cooler coils.

The breaking down of abietic acid into abietene according to the equation  $C_{19}H_{28}O_2 = C_{18}H_{26} + CO_2$  takes place rapidly in iron retorts, far more slowly in glass vessels. This difference is so marked that, whereas the resin acid is conveniently purified by distillation from glass vessels under pressures below 100 mm., it cannot be so purified even under 20 mm. in the presence of metallic iron.

Morris (*Proc.*, 1889, 70, 102) has thrown doubt on Kelbe's statement that the hydrocarbon obtained from resin oil by distillation with sulphur is retene. According to Morris, when colophony is distilled with sulphur, a hydrocarbon melting at  $84-85^\circ$  results. Experiment has shown that the distillation of abietene with a small amount of sulphur under atmospheric pressure or with much sulphur under reduced pressure yields retene. With much sulphur under the ordinary pressure, a hydrocarbon melting at  $86^\circ$  results, together with a compound boiling at about  $320^\circ/30$  mm., which is very sparingly soluble in hot alcohol. The compound melting at  $86^\circ$  and also a compound having a very high boiling point result if retene itself is distilled with sulphur under atmospheric pressure.

## EXPERIMENTAL.

*Distillation of Colophony under Diminished Pressure. Non-existence of isosylvic Anhydride.*

According to Bischoff and Nastvogel (*Ber.*, 1890, 23, 1921), colophony, on distillation under reduced pressure, yields the anhydride of *isosylvic* acid. The following experiment shows that the distillate consists chiefly of abietic acid: 400 grams of American colophony ("N quality") were distilled from an ordinary distilling flask under 31 mm. pressure, and the portion boiling at 270—290° (222 grams) was fractionated five times under pressures varying from 27 to 35 mm. Analysis of the distillates gave numbers agreeing with those required for abietic acid.

Calculated for <i>isosylvic</i> anhydride.	Calculated for abietic acid.	Found. Distillates.				
		1st.	2nd.	4th.	5th.	6th.
C = 81.9	79.16	79.8	78.8	78.7	78.8	78.9
H = 9.9	9.72	9.9	9.6	9.5	9.8	9.7

The first and sixth distillates were dissolved in hot 80 per cent. alcohol; the solutions, on cooling, deposited a large crop of crystals having the characteristic form of abietic acid, which, after two crystallisations, melted at 163—165°.

According to Bischoff and Nastvogel, *isosylvic* anhydride dissolves almost completely in caustic alkali, and when reprecipitated yields *isosylvic* acid melting at 61—63°. The sixth distillate was accordingly dissolved in dilute caustic potash, with which it formed a clear solution; after shaking out with ether, which removed a small quantity of hydrocarbon, the last traces of ether were removed by evaporation, and the cold alkaline solution was precipitated by dilute acetic acid. Two preparations of the precipitated acid melted at 65—73° and at 67—80°. The latter was dissolved in hot 80 per cent. alcohol, from which it separated in triangular plates melting at 160—165°.

The explanation of these results is a simple one: abietic acid precipitated from its solution in alkalis is amorphous, and its melting point follows the general rule of being lower than that of the crystalline form of the same substance.

Colophony, purified by distillation as above, is a very light amber-coloured substance. When quickly cooled, it sets to a resin, which does not crystallise even after three years.\* It has no definite

\* (The original specimens were prepared and analysed in September, 1900.—T. H. E.)

melting point; if melted and kept for twenty-four hours slightly above the temperature of complete fusion, it sets to a mass of crystals.

By distilling colophony under diminished pressure, crude abietic acid may be conveniently obtained in a state of comparative purity. For obtaining the volatile resin acids in quantity, however, recourse has been had to the distillation in superheated steam, a process patented by Hunt and Pochin in 1858.

### *Distillation of Colophony in Superheated Steam.*

Colophony (1655 lbs.) was introduced into a three-ton stearin still and superheated steam was blown through the molten mass. When the temperature of the still had reached  $268^{\circ}$ , an oily distillate began to run from the first coil. Most of the resin came over between  $300^{\circ}$  and  $310^{\circ}$ , and within these limits the distillate from the first two coils was practically colourless, and set on cooling to a hard, brittle resin. Above  $310^{\circ}$  the distillate began to darken in colour and to come over more slowly, and at  $330^{\circ}$  the distillation was stopped. During the whole distillation, the material from the third, fourth, and fifth coils was opaque, and did not become hard when cooled. The following quantities were obtained: 63 per cent. of hard distillate which crystallised when slowly cooled, and 26 per cent. of soft distillate containing 20 per cent. of resin oil.

The examination of the products is still proceeding.

### *Abietene.*

During the redistillation of colophony, a small quantity of an oily hydrocarbon is formed, even although the pressure is reduced to 11 mm.; above 100 mm. pressure, the quantity of oil is so great that the distillate does not become hard when cooled. The occurrence of this oil was noticed by Bischoff and Nastvogel, who regarded it as being probably a diterpene, possibly identical with "colophene." The structural formulæ suggested by these authors show that they regarded the hydrocarbon as the parent substance from which *isosylvic* acid was derived by oxidation. It appeared more probable that the hydrocarbon was derived from the acid by a mere elimination of carbon dioxide, and this supposition was strengthened by the observation that the hydrocarbon is obtained more readily if colophony is distilled from an iron still rather than from a glass one.

Thirty-six grams of crystallised abietic acid were mixed with a small quantity of iron filings and slowly distilled from a four-bulb Ladenburg flask under 30 mm. pressure. The temperature of the

uppermost bulb was readily kept at 210—220°, and the distillate consisted of a faintly fluorescent, viscid oil. After three hours' heating, the contents of the flask had become so viscid (ketone formation?) that the distillation could not be continued without decomposition. The distillate, which now amounted to 44 per cent. of the weight of abietic acid taken, was freed from acids by means of caustic soda, and eventually distilled over sodium. Practically the whole came over at 200—215°/19 mm., and when redistilled under 82 mm. pressure, the greater portion boiled at 247—250°.

Found, C=88·3. H=11·7.

$C_{18}H_{28}$  requires C=88·5; H=11·5 per cent.

The molecular weight determined by Mr. P. W. Robertson in phenolic solution gave 244 and 249, taking 72 as the depression constant for phenol (Eykmán):  $C_{18}H_{28}$  requires 244.

No other volatile products of the distillation could be detected, with the exception of a few drops of discoloured water, although a second receiver surrounded by a freezing mixture was attached to the distilling apparatus during the whole operation.

Abietene was also readily obtained by distilling colophony from an iron retort provided with a rod and disc fractionating column, the pressure being reduced to 15—35 mm., whilst the temperature of the still head was 215—230°. The composition of the distillate was as follows:

Unaltered acid .....	14·0 per cent.
Oil, b. p. 241—250° under 85 mm.	8·3 „ „
„ „ 250—253° „ „	63·7 „ „
„ „ 256—272° „ „	7·0 „ „
Residue .....	3·9 „ „
Loss .....	3·1 „ „
	<hr/>
	100·0 „ „

The portion boiling at 250—253° was repeatedly distilled from sodium, when different preparations gave the following analytical results:

	Found.			$C_{18}H_{28}$ requires :
C = 88·3	88·2	88·6		88·5 per cent.
H = 11·1	10·9	11·2		11·5 „ „

The hydrocarbon is again easily obtained by slowly distilling colophony from glass retorts under atmospheric pressure, and then repeatedly fractionating the complicated mixture of products under

diminished pressure. The following table shows that the abietene obtained by the different methods is the same hydrocarbon :

Origin of abietene.	Crystallised abietic acid.	Colophony in iron still under 15—35 mm. pressure.	Colophony in glass retort under 755 mm. pressure.	Colophony on dis- tillation in steam.
Specific gravity (18—19°).	0.9728	0.9727	0.976	0.975
Refractive index (Abbé).	1.537	1.538	1.539	1.529
B. p. 247—250 (82 mm.).	$\left. \begin{array}{l} 199-200^{\circ} (13 \text{ mm.}) \\ 253-255^{\circ} (82-85 \text{ mm.}) \\ 340-345^{\circ} (760 \text{ mm.}) \end{array} \right\}$			

The abietene prepared from colophony in the iron still was found to have  $[\alpha]_D = 92.9^{\circ}$ .

Abietene rapidly absorbs about 9 per cent. of its own weight of oxygen when exposed to the air in thin layers, this absorption being accompanied by a great increase in viscosity. With wet slaked lime, the hydrocarbon forms a grease, in which respect it resembles commercial resin oil, of which it is no doubt an important constituent.

#### *Action of Hydriodic Acid on Abietic Acid.*

The following experiments demonstrate that the interaction between abietic and hydriodic acids does not lead to the formation of a terpene, but that abietene is produced and a carboxyl group eliminated :

1. Five grams of recrystallised abietic acid were heated with 20 c.c. of fuming hydriodic acid for six hours at 210—230°. The resulting hydrocarbon distilled almost entirely between 245° and 255° under 84 mm. pressure, and gave the following numbers : C = 88.2 ; H = 10.9 ; sp. gr. = 0.962 ;  $n_D = 1.532$ , which agree closely with those already indicated for abietene.

2. Two grams of abietic acid were heated with 10 c.c. of fuming hydriodic acid at 200—210° for two hours in a sealed tube, the pressure in which had been previously reduced to 20 mm. The gases formed were collected over water and analysed, no account being taken of their solubility. The corrected volume of the gas was 143 c.c., and this contained 80.6 per cent. of carbon monoxide and 8.8 per cent. of carbon dioxide, or 89.4 per cent. of gases derived from a carboxyl group ; this proportion corresponds with more than 80 per cent. of the volume of the oxides of carbon theoretically obtainable from two grams of abietic acid.

In a strictly comparable experiment, in which hydrochloric acid of the same equivalent strength was substituted for the hydriodic acid, only a few cubic centimetres of gas were obtained.

*Dihydroabietene.*

Ten grams of freshly rectified abietene were reduced with hydriodic acid and excess of phosphorus at 220—240° for four hours. The product, which was a colourless hydrocarbon having a beautiful blue fluorescence and boiling for the most part between 330° and 340°, had a sp. gr. 0.933 and  $n_D = 1.522$ . Analysis agrees with the supposition that the compound is dihydroabietene.

Found, C = 87.7. H = 12.3.

$C_{18}H_{30}$  requires C = 87.8 ; H = 12.2 per cent.

The hydrocarbon which Liebermann (*Ber.*, 1884, 17, 1885) obtained by reducing sylvic (abietic) acid with hydriodic acid and phosphorus boiled at 320—330°, and gave on analysis C = 87.5, H = 12.4 (mean of two analyses).

According to Liebermann and Spiegel, dodecahydoretene boils at 336° (*Ber.*, 1889, 22, 780) and shows a beautiful blue fluorescence ; it is very probable that dihydroabietene and dodecahydoretene are identical. Unlike abietene, the dihydro-compound shows no increase in weight or viscosity when exposed to the air in thin layers for forty-eight hours.

*Retene from Abietene.*

According to Kelbe (*Abstr.*, 1888, 54, 605), resin oil yields retene if distilled with sulphur. Morris (*Proc.*, *loc. cit.*), however, states that the distillation of colophony with sulphur yields a hydrocarbon which melts at 84—85°, and is not retene. Quite recently, Vesterberg (*Ber.*, 1903, 36, 4200) has made the interesting observation that abietic acid yields retene if distilled with half its weight of sulphur under diminished pressure. The following observations are of interest in connection with the apparently conflicting statements of the various authors.

(1) Ten grams of abietene, heated with one-third of its weight of sulphur until evolution of gas ceased and then distilled under atmospheric pressure, gave a dark, viscid distillate which was redistilled under reduced pressure (80 mm.). The portion boiling at 260—280° solidified on cooling, and after thrice crystallising from alcohol melted at 97—99°, and did not perceptibly affect the melting point of a specimen of "retene puriss," supplied by Merck, when the two hydrocarbons were mixed in approximately equal proportion.

(2) Abietene (65 grams), heated with two-thirds its weight of sulphur (the quantity theoretically required to oxidise abietene to retene), gave 26.5 grams of distillate, which crystallised on cooling.

Distillation of the product under reduced pressure now gave the following fractions: (1) 2.7 grams, b. p. 250—280°/87 mm.; (2) 14.8 grams, b. p. 260—290°/70 mm.; (3) 7.5 grams, b. p. 290—360°/70 mm.

The most volatile distillate did not solidify. The middle fraction crystallised readily; after two crystallisations from alcohol, it melted at 86°, and the melting point was not altered by sublimation followed by crystallisation from alcohol. The sublimed hydrocarbon superfuses readily, is quite colourless, and is surprisingly like retene in appearance and solubility in alcohol; it also appears to have the same composition.

Found, C = 92.26. H = 7.67.

$C_{18}H_{18}$  requires C = 92.3; H = 7.7 per cent.

The third fraction is sparingly soluble in boiling alcohol and has not been further examined.

3. Ten grams of abietene, heated with half its weight of sulphur until the temperature reached 250° and then distilled under 27 mm., gave a considerable quantity of distillate boiling at 230—260°, and a smaller fraction passing over from 260—320°. The more volatile fraction was twice recrystallised from alcohol and melted at 98—99°, leaving little doubt that it was retene.

It appeared possible that the formation of the hydrocarbon melting at 86° and of the substance boiling above 290°/70 mm. might be due to the action of sulphur on the retene which is first formed. The results of the following experiment strongly support this view.

Ten grams of retene (Merck) were distilled with two grams of sulphur under atmospheric pressure, and the distillate fractionated under reduced pressure. A fraction, having a high boiling point and sparingly soluble in alcohol, was obtained together with a larger quantity of a comparatively volatile distillate. The latter consisted largely of unaltered retene melting at 97—99°, but from the mother liquors the hydrocarbon was obtained in small quantity, melting constantly at 86°.

The interaction between retene and sulphur and that between abietene and sulphur are being further examined, but as Vesterberg has notified that he is investigating the action of sulphur on the resins and diterpenes as a class, the authors do not propose to extend their work in this direction.

The authors would remark that the observations recorded in this paper do not lend support to the popular view that abietic acid is an oxidation product of the terpenes. They venture to suggest that the terpenes are employed as solvents in which the resins are

removed from the plant system, and that this is the true meaning of the constant association of the two classes of compounds.

In conclusion, the authors would express their thanks to Messrs. John Newton and Son, of the Kaiwarrawarra Soapworks, and to the directors and staff of the New Zealand Candle Co., for the opportunity afforded them of investigating the distillation of colophony in superheated steam on a manufacturing scale.

A portion of the expense of the above investigation has been borne by a grant from the research fund of the Royal Society.

VICTORIA COLLEGE,  
WELLINGTON, N.Z.

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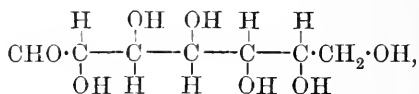
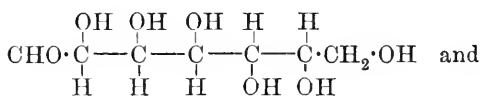
CXXVII.—*Studies in Asymmetric Synthesis. I. Reduction of Menthyl Benzoylformate. II. Action of Magnesium Alkyl Haloids on Menthyl Benzoylformate.*

By ALEXANDER MCKENZIE.

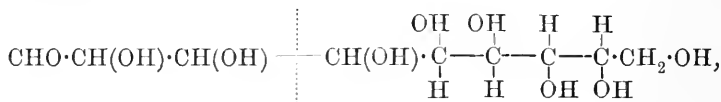
It is well known that various optically active substances, of which *d*-glucose, *d*-fructose, *d*-tartaric acid, and *l*-malic acid are common types, occur in nature as products of plant or animal metabolism. They do not, however, occur as a mixture of two enantiomorphous forms in unequal amounts, but in the pure enantiomorphous form; thus *l*-glucose is not found in nature associated with *d*-glucose, nor is *l*-fructose found associated with *d*-fructose. With reference to the mode of formation of such compounds, it is improbable that their optical activity is due to the initial synthesis of the inactive form and its subsequent resolution by an asymmetric agent, with the total destruction of the one enantiomorphous form and the survival of the other. The conception of asymmetric synthesis, on the other hand, first introduced by Emil Fischer, and based by him on experiments with substances of definite constitution, meets with most favour. In the case, for instance, of the synthesis of *d*-glucose in the leaves of plants, it is assumed that the chlorophyll, which is presumably optically active, exerts a directive influence on the condensation of carbon dioxide or formaldehyde of such a kind that the sugar formed is also active (*Ber.*, 1894, 27, 3231); the chlorophyll and sugar may possibly form an additive compound, which is disrupted with the regeneration of the original chlorophyll complexes and the elimination of an optically active sugar. In support

of this view, Fischer cites experimental evidence from the syntheses he accomplished by aid of the cyanohydrin reaction. In the formation of gluco-octonic acids, the yield of the  $\alpha$ - is much greater than that of the  $\beta$ -acid; a similar result is obtained in the synthesis of rhamnohexonic acid; with mannoheptonic acid, the yield of the  $\alpha$ -acid is as much as 87 per cent. of the theory, whilst no trace of the  $\beta$ -isomeride was detected (*Ber.*, 1889, 22, 370; *Annalen*, 1892, 270, 68). To make the idea clearer, the following instance is quoted by Fischer and Slimmer (*Sitzungsber. K. Akad. Wiss. Berlin*, 1902, 28, 597). Mannose with

the configuration  $\text{CHO} \cdot \overset{\text{OH}}{\underset{\text{H}}{\text{C}}} - \overset{\text{OH}}{\underset{\text{H}}{\text{C}}} - \overset{\text{H}}{\underset{\text{OH}}{\text{C}}} - \overset{\text{H}}{\underset{\text{OH}}{\text{C}}} \cdot \text{CH}_2 \cdot \text{OH}$  might be expected to yield, by the cyanohydrin reaction, the two isomeric mannoheptoses,



but, as a matter of fact, only one of them is formed. From this heptose again, by the further application of the cyanohydrin reaction, only one of the two possible octoses has been isolated, and this octose was also found to yield only one nonose. If now the molecule of mannnononose, synthesised in the manner just indicated, be represented as follows:

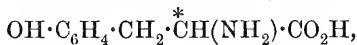


and if it could possibly be degraded at the point indicated by the dotted line, it might be expected that the original active mannose would be regenerated and an active glyceric aldehyde formed.

All attempts to realise an asymmetric synthesis on the lines indicated by Fischer have, however, been hitherto unsuccessful. Thus, although helicin forms a crystalline cyanohydrin which has all the appearance of a uniform substance, it was not found possible to prepare from it salicylaldehydecyanohydrin owing to the ease with which the latter is hydrolysed (E. Fischer, *Ber.*, 1901, 34, 629). Cohen and Whiteley (*Trans.*, 1901, 79, 1305) studied the dibromo-derivatives of amyl and menthyl cinnamates and the reduction of the menthyl esters of mesaconic,  $\alpha$ -methylcinnamic, and pyruvic acids, whilst Kipping (*Proc.*, 1900, 16, 226) examined the reduction of the bornyl esters of

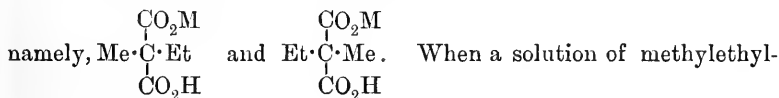
pyruvic, lævulinic, and benzoylformic acids and the reduction of the quinine salts of pyruvic and lævulinic acids. Fischer and Slimmer (*Sitzungsber. K. Akad. Wiss. Berlin*, 1902, 28, 597; *Ber.*, 1903, 36, 2575) studied the formation of *o*-hydroxymandelic acid and of *o*-hydroxyphenylethylcarbinol from tetra-acetylhelicin.

Fischer has afforded further evidence of the preferential formation of one isomeride before another under asymmetric influence in his recent syntheses of polypeptides (*Ber.*, 1904, 37, 2486). For example, *i*- $\alpha$ -bromoisocapronyl chloride,  $C_4H_9 \cdot \overset{*}{CH}Br \cdot COCl$ , which contains one asymmetric carbon atom, combines with *l*-tyrosine,



which also contains one asymmetric carbon atom, to form  $\alpha$ -bromoisocapronyl-*l*-tyrosine,  $C_4H_9 \cdot \overset{*}{CH}Br \cdot CO \cdot NH \cdot \overset{*}{CH}(CH_2 \cdot C_6H_4 \cdot OH) \cdot CO_2H$ , containing two asymmetric carbon atoms. Now it might be expected that two stereoisomerides of the latter type should be formed, but the product obtained by Fischer behaved like a uniform substance, although, as he points out, it may nevertheless be a mixture of the two modifications should they form mixed crystals with one another (compare E. Fischer and Suzuki, *Ber.*, 1904, 37, 2843).

The first asymmetric synthesis has lately been effected by Marckwald (*Ber.*, 1904, 37, 349), who based his experiments on a conception different from that which guided previous investigators. Whilst two series of hydrogen sulphites, represented by  $M \cdot SO_2 \cdot OH$  and  $H \cdot SO_2 \cdot OM$ , respectively, are theoretically possible, it is found that from such unsymmetrical dibasic acids only one hydrogen salt with one and the same base can be isolated. Methylethylmalonic acid,  $CMeEt(CO_2H)_2$ , does not contain an asymmetric carbon atom, but when one of the replaceable hydrogen atoms is substituted by a metal, the carbon atom becomes asymmetric and two enantiomorphous salts are possible,



malonic acid, which has been half neutralised by an inactive base like potassium hydroxide, is evaporated, an inactive product (either the *dl*-mixture or the *r*-salt) separates, since the solubility of the two types under consideration is the same. On the other hand, when an active base is employed, the two salts are no longer mirror-images and, on evaporation of the solution, only one salt separates with re-establishment of equilibrium between the two salts in solution. Marckwald accordingly obtained the brucine hydrogen salt of methylethylmalonic acid, which, when heated at  $170^\circ$ , lost carbon dioxide and was converted into the brucine salt of methylethylacetic acid. The acid,

obtained after removal of the brucine from the latter salt, was a mixture of *dl*- and *l*-methylethylacetic acids, containing 10 per cent. of the latter.

Cohen and Patterson (*Ber.*, 1904, 37, 1012) do not consider this synthesis of active valeric acid to be an asymmetric one, since a solution of methylethylmalonic acid is regarded by them as containing

the enantiomorphous ions,  $\text{Me} \cdot \overset{\text{CO}_2'}{\underset{\text{CO}_2\text{H}}{\text{C}}} \cdot \text{Et}$  and  $\text{Et} \cdot \overset{\text{CO}_2'}{\underset{\text{CO}_2\text{H}}{\text{C}}} \cdot \text{Me}$ , that is, the

acid in solution already contains an asymmetric carbon atom before the active brucine enters into reaction with it. In reply to their criticism, Marekwald (*Ber.*, 1904, 37, 1368), after giving a precise definition of an asymmetric synthesis as follows, "Asymmetrische Synthesen sind solche, welche aus symmetrisch constituirten Verbindungen unter intermediärer Benutzung optisch-activen Stoffe, aber unter Vermeidung jedes analytischen Vorganges, optisch-active Substanzen erzeugen," points out that the brucine hydrogen salt of methylethylmalonic acid is formed in quantitative yield, that no analytical separation is necessary, and that the salt may be produced in non-ionising solvents, such as ether or chloroform.

In the present communication, evidence is submitted to indicate the accomplishment of a successful asymmetric synthesis on the lines laid down by Fischer.

The preparation of *l*-menthyl *dl*-mandelate from *r*-mandelic acid and *l*-menthol by the hydrogen chloride method was described in a previous paper (McKenzie, *Trans.*, 1904, 25, 378). When this ester is hydrolysed by an excess of alcoholic potassium hydroxide, it yields, of course, *r*-mandelic acid. When it is hydrolysed, however, by an amount of potassium hydroxide insufficient for complete hydrolysis, an optically active mandelic acid is invariably obtained from the potassium salt so formed; when the mixture of esters still remaining after this partial hydrolysis is then completely hydrolysed, the mandelic acid obtained is either optically active or inactive according to the conditions under which this final hydrolysis is conducted. The presence of a considerable excess of alkali is found to favour the formation of an inactive acid. Accordingly, in the complete hydrolysis by potassium hydroxide of a mixture of *l*-menthyl *d*-mandelate and *l*-menthyl *l*-mandelate containing an excess of either of these esters, racemisation phenomena come into play, since the acid obtained is not always optically active.

Now the asymmetric synthesis of mandelic acid might be attempted by reducing menthyl benzoylformate,  $\text{PhCO} \cdot \text{CO}_2 \cdot \text{C}_{10}\text{H}_{19}$ , to menthyl mandelate,  $\text{PhCH}^*(\text{OH}) \cdot \text{CO}_2 \cdot \text{C}_{10}\text{H}_{19}$ , hydrolysing the latter and then removing the *l*-menthol. When this experiment was performed, the mandelic

acid obtained was inactive, as was fully expected from the racemisation phenomena described in the paper just referred to. But it does not at all follow from this result that equal amounts of *l*-menthyl *d*-mandelate and *l*-menthyl *l*-mandelate were present in the product obtained by the reduction of menthyl benzoylformate, since, had unequal amounts been present, the mandelic acid obtained might still have been inactive owing to the racemising effect of the alkali during hydrolysis of the esters. In order, therefore, to have some idea of the relative amounts of the two esters produced in the reaction in question, these esters themselves were prepared from *d*- and *l*-mandelic acids respectively. *l*-Menthyl *d*-mandelate melts at 99—100° and has  $[\alpha]_D^{10} - 7.6^\circ$  ( $c = 3.5956$ ) in ethyl-alcoholic solution, whilst *l*-menthyl *l*-mandelate melts at 81—82° and has  $[\alpha]_D^{17} - 138.6^\circ$  ( $c = 4.3732$ ) in ethyl-alcoholic solution. *l*-Menthyl *dl*-mandelate, prepared from *r*-mandelic acid (*loc. cit.*), melts at 85—86° and has  $[\alpha]_D^{18} - 74.2^\circ$  in ethyl-alcoholic solution, a value sufficiently close to that calculated from the figures for the esters of the active acids, namely,  $-73.1^\circ$ . The product, obtained by the reduction of menthyl benzoylformate, gave in one experiment  $[\alpha]_D^{18} - 76.9^\circ$  ( $c = 6.174$ ), and in another  $[\alpha]_D^{20} - 77.6^\circ$  ( $c = 2.558$ ), results which indicated that a slight excess of *l*-menthyl *l*-mandelate was present.

Distinct evidence of asymmetric synthesis was, however, afforded when the Grignard reaction was applied to menthyl benzoylformate. Grignard has shown (*Compt. rend.*, 1902, 135, 627; *Ann. Chim. Phys.*, 1902, [vii], 27, 548) that when a magnesium alkyl bromide,  $MgR'R$ , for example, acts on a compound of the type  $RCO \cdot CO_2Et$ , the first phase of the reaction consists in the formation of the compound  $CRR'(O \cdot MgBr) \cdot CO_2Et$ , which, when acted on by water, forms  $CRR'(OH) \cdot CO_2Et$ , an ester of a hydroxy-acid; in the second phase, the reaction proceeds further to give  $CRR'(O \cdot MgBr) \cdot C(O \cdot MgBr)R'R'$ , which, when acted on by water, gives  $CRR'(OH) \cdot C(OH)R'R'$ , a ditertiary glycol. The experimental conditions may, however, be so chosen that the reaction is restricted to the first phase, the carbonyl grouping in esters of ketonic acids being much more reactive towards Grignard's reagent than the carboxyalkyl grouping.

When menthyl benzoylformate,  $PhCO \cdot CO_2 \cdot C_{10}H_{19}$ , is acted on by magnesium methyl iodide and the magnesium additive compound then decomposed by water and dilute acid, a new asymmetric carbon atom is produced. When the resulting compound,  $^*CMePh(OH) \cdot CO_2 \cdot C_{10}H_{19}$ , is hydrolysed, no racemising effects are observed in this case, since an optically active salt is present in solution after the complete removal of the *l*-menthol, and this salt yields an optically active phenylmethylglycollic acid,  $^*CMePh(OH) \cdot CO_2H$ . Magnesium ethyl bromide behaves similarly.

A confirmation of the fact that the activity observed with these substituted glycollic acids was actually due to their asymmetric synthesis was afforded by the formation of benzilic acid,  $\text{CPh}_2(\text{OH})\cdot\text{CO}_2\text{H}$ , from menthyl benzoylformate and magnesium phenyl bromide. In this case, an additional phenyl group was introduced into the molecule of menthyl benzoylformate, but a new asymmetric carbon atom was not produced, and the result was that the potassium salt, obtained after removal of the menthol, was inactive, as was also the corresponding acid.

### EXPERIMENTAL.

*Menthyl benzoylformate* is conveniently prepared as follows.

Benzoylformic acid, obtained by the oxidation of acetophenone by alkaline potassium permanganate, was heated on a boiling water-bath with three times its weight of *l*-menthol for 9—10 hours, a current of dry hydrogen chloride being passed into the mixture at intervals of three hours. The ethereal solution of the product was then washed, first with water and afterwards with dilute sodium carbonate solution, after which the ether was expelled and the residue submitted to steam distillation until the menthol had nearly all been removed. The oil remaining after this treatment soon solidified and was then crystallised from ethyl alcohol, in which it is moderately soluble and from which it separates in glassy needles melting at 73—74°.

0.1982 gave 0.1538  $\text{H}_2\text{O}$  and 0.5434  $\text{CO}_2$ .  $\text{H} = 8.6$ ;  $\text{C} = 74.8$ .

$\text{C}_{18}\text{H}_{24}\text{O}_3$  requires  $\text{H} = 8.3$ ;  $\text{C} = 75.0$  per cent.

The specific rotation of the ester was determined in ethyl-alcoholic solution:

$$l = 2, c = 4.7832, \alpha_D^{20} - 4.25^\circ, [\alpha]_D^{20} - 44.4^\circ.$$

*l*-Menthyl *d*-mandelate was prepared from *d*-mandelic acid, obtained by the resolution of the *r*-acid by cinchonine, the method used being similar to that just described for menthyl benzoylformate. Steam distillation may also in this case be used for separating the menthol, since the ester undergoes no appreciable hydrolysis when boiled with water. *l*-Menthyl *d*-mandelate separates from ethyl alcohol in rectangular plates and melts at 99—100°.

0.2028 gave 0.1648  $\text{H}_2\text{O}$  and 0.5500  $\text{CO}_2$ .  $\text{H} = 9.0$ ;  $\text{C} = 74.0$ .

$\text{C}_{18}\text{H}_{26}\text{O}_3$  requires  $\text{H} = 9.0$ ;  $\text{C} = 74.4$  per cent.

The specific rotation was determined in ethyl-alcoholic solution:

$$l = 2, c = 3.5956, \alpha_D^{10} - 0.55^\circ, [\alpha]_D^{10} - 7.6^\circ.$$

*l*-Menthyl *l*-mandelate, prepared from *l*-mandelic acid, obtained from

amygdalin, separates from ethyl alcohol in long, glassy needles and melts at 81—82°. It was analysed by hydrolysis with standard alcoholic potassium hydroxide :

0.3226 required 0.0622 potassium hydroxide for complete hydrolysis, the theoretical amount being 0.0623.

The specific rotation was determined in ethyl-alcoholic solution :

$$l = 2, c = 4.3732, \alpha_D^{17^\circ} - 12.12^\circ, [\alpha]_D^{17^\circ} - 138.6^\circ.$$

Its *benzoyl* derivative, prepared by the Schotten-Baumann method, separates from ethyl alcohol in glassy, rectangular plates and melts at 54—55°. Its specific rotation in ethyl alcohol was determined :

$$l = 2, c = 4.2888, \alpha_D^{16^\circ} - 10.28^\circ, [\alpha]_D^{16^\circ} - 119.8^\circ.$$

When equal weights of *l*-menthyl *d*-mandelate and *l*-menthyl *l*-mandelate were dissolved in ethyl alcohol and mixed, and the alcohol then evaporated off, the product obtained was identical in appearance and properties with the partially racemic *l*-menthyl *dl*-mandelate previously described (*loc. cit.*). It melted at 86—86.5° and had the following rotation in ethyl-alcoholic solution :

$$l = 2, c = 3.1632, \alpha_D^{21^\circ} - 4.66^\circ, [\alpha]_D^{21^\circ} - 73.6^\circ.$$

From the results obtained by the author in connection with the fractional hydrolysis of *l*-menthyl *dl*-mandelate (*loc. cit.*), which in solution may be regarded as consisting of equal amounts of *l*-menthyl *d*-mandelate and *l*-menthyl *l*-mandelate, it had been concluded that unusual racemisation phenomena must occur during the hydrolysis of the latter esters by alkali. Further opportunity of studying this case has now been afforded by hydrolysing the individual esters, isolated as above described. After it had been observed that the resulting potassium salt was inactive when either of the esters was hydrolysed by boiling with a large excess of alcoholic potassium hydroxide, the hydrolyses were next conducted under such conditions as might be expected to yield a mandelic acid of the maximum activity. It was curious to find that in every case a partially racemised mandelic acid resulted.

*l*-Menthyl *l*-mandelate (1.5 grams) was dissolved in 30 c.c. of ethyl alcohol, and 4.2 c.c. of alcoholic potassium hydroxide (the calculated amount, 1 c.c. = 0.06935 KOH) added, the mixture being then heated in a reflux apparatus for two hours. The alcohol was then expelled, the residual oil treated with water, and the menthol removed. The neutral filtrate was acidified and extracted with ether. The mandelic acid obtained melted at 114—117° and

a determination of its specific rotation in aqueous solution gave the following result :

$$l=2, c=2.7208, \alpha_D - 1.56^\circ, [\alpha]_D - 28.7^\circ,$$

whereas *l*-mandelic acid melts at  $133^\circ$  and has  $[\alpha]_D$  about  $-156^\circ$ .

Very marked racemisation also took place when the hydrolysis was conducted at a temperature lower than in the preceding case: 1.3 grams of the ester were hydrolysed by 50 c.c. of alcoholic potassium hydroxide, containing the calculated amount of alkali, by being kept in a thermostat for 42 hours at  $25^\circ$ , after which time the hydrolysis was complete. The neutral solution was manipulated as before; the mandelic acid obtained had the following rotation in aqueous solution :

$$l=2, c=1.928, \alpha_D^{20^\circ} - 1.40^\circ, [\alpha]_D^{20^\circ} - 36.3^\circ.$$

When the hydrolysis is conducted with the calculated amount of aqueous sodium hydroxide of about *N*/30 strength, the action proceeds very slowly, even at the temperature of the boiling water-bath, and the racemisation is not nearly so pronounced: 0.908 gram of ester was taken, an amount which required for complete hydrolysis 94.4 c.c. of the aqueous sodium hydroxide used. Fifty c.c. of this solution were first added, and after two days at  $25^\circ$  the solution still had an alkaline reaction. The mixture was then heated on the boiling water-bath for 9 hours, when the solution was still slightly alkaline. After 12 hours at the ordinary temperature, 44 c.c. of the sodium hydroxide solution were further added and the heating continued for 14 hours, at the end of which time the solution was practically neutral. The acid recovered gave the following result :

$$l=2, c=0.9452, \alpha_D^{19^\circ} - 2.39^\circ, [\alpha]_D^{19^\circ} - 126.4^\circ.$$

Although *l*-menthyl *d*-mandelate and *l*-menthyl *l*-mandelate are hydrolysed at different rates, the acids obtained when the esters are separately hydrolysed under exactly the same conditions by slightly more than the calculated amount of alcoholic potassium hydroxide possess the same numerical value: 1.9216 grams of each ester were dissolved in 25 c.c. ethyl alcohol and 30 c.c. of alcoholic potassium hydroxide (1 c.c. = 0.01386 gram KOH) were added, the calculated amount being 26.8 c.c. After remaining at  $25^\circ$  for 27 hours, the acid was obtained in the usual manner from each solution. The dextro-rotatory acid had the following specific rotation :

$$l=2, c=3.2232, \alpha_D^{20.5^\circ} + 2.89^\circ, [\alpha]_D^{20.5^\circ} + 44.8^\circ,$$

whilst the laevorotatory acid had

$$l=2, c=3.3352, \alpha_D^{20.5^\circ} - 2.97^\circ, [\alpha]_D^{20.5^\circ} - 44.6^\circ$$

The extent to which racemisation took place is accordingly the same in both cases.

*Reduction of Menthyl Benzoylformate.*

Two grams of menthyl benzoylformate were dissolved in 75 c.c. of ether containing a little water. After remaining for 24 hours in contact with an excess of aluminium amalgam, the mixture was filtered and the filtrate evaporated to dryness. The substance obtained in this manner had the asbestos-like appearance of *l*-menthyl *dl*-mandelate; it melted at 85–86° and was analysed by hydrolysis with standard alcoholic potassium hydroxide.

0.3905 required 0.0754 potassium hydroxide for complete hydrolysis, the theoretical amount being 0.0758.

A determination of its specific rotation in ethyl alcohol gave the following result:

$$l = 2, c = 6.174, \alpha_D^{18} - 9.49^\circ, [\alpha]_D^{18} - 76.9^\circ.$$

In a second experiment, where an ethyl-alcoholic solution of menthyl benzoylformate was left in contact with aluminium amalgam for several days, the product obtained melted at 83–85° and had the following rotation in ethyl-alcoholic solution:

$$l = 2, c = 2.558, \alpha_D^{20} - 3.97^\circ, [\alpha]_D^{20} - 77.6^\circ.$$

When the reduction products from these two experiments were respectively hydrolysed by heating with a slight excess of alcoholic potassium hydroxide, inactive mandelic acid, melting at 119°, was obtained from the potassium salt in each case.

When menthyl benzoylformate in ethyl-alcoholic solution was acted on by sodium amalgam and glacial acetic acid, a product was obtained which melted indistinctly at 65–78° and had  $[\alpha]_D^{20} - 64.0^\circ$  ( $c = 4.4172$ ) in ethyl-alcoholic solution. The reduction was probably incomplete, and some unchanged menthyl benzoylformate was probably present, although, when the product was crystallised twice from aqueous ethyl alcohol, the rotation was much the same as before, namely,  $[\alpha]_D^{20} - 63.2^\circ$  ( $c = 2.7428$ ). On hydrolysis, inactive mandelic acid was again produced.

*Action of Magnesium Ethyl Bromide on Menthyl Benzoylformate.*

Magnesium (0.61 gram =  $1\frac{1}{2}$  mols.) was added to a mixture of 3 grams of ethyl bromide ( $1\frac{1}{2}$  mols.) and 40 c.c. of ether with the usual precautions to ensure dryness. When the magnesium had almost all

dissolved, the solution was gradually added, within an interval of 7 minutes, to a solution of 5 grams of menthyl benzoylformate (1 mol.) in 40 c.c. of dry ether. The temperature of the mixture rose slightly, but the reaction was never a vigorous one. After half an hour at the temperature of the laboratory, the product was heated on the water-bath for two hours and then left overnight. After the addition first of water and then of dilute hydrochloric acid, the ethereal solution was separated and washed once with water. The ether was next expelled and a product obtained, which remained as a viscid oil after having been left for several days in a partial vacuum over sulphuric acid. The oil was dissolved in 45 c.c. of ethyl alcohol and 17 c.c. of alcoholic potassium hydroxide (1 c.c. = 0.0606 gram KOH) were added and the mixture boiled for 1 hour. After expulsion of the alcohol, water was added to the oil, and the menthol, which separated as a solid, drained off. The filtrate was then completely freed from menthol by evaporating to a small bulk and then extracting with ether (although the extraction with ether is really unnecessary). The aqueous solution of potassium salt was acidified and the acid extracted with ether. The acid, obtained after evaporation of the ether, was an oil, which, after remaining for a night in a vacuum over sulphuric acid, had begun to crystallise in tiny, rectangular plates grouped in rosettes. It was moderately soluble in water. When dissolved in ethyl alcohol and made up to 8 c.c., a volume sufficient to fill the 1 dcm. tube employed, the acid was found to be distinctly lævorotatory, giving  $\alpha_D^{19^\circ} - 1.03^\circ$ . It formed a zinc salt which was lævorotatory, and which, when dried at  $130-140^\circ$ , gave, on analysis, 15.3 per cent. of zinc, whereas zinc phenylethylglycollate,  $C_{20}H_{22}O_6Zn$ , requires 15.4 per cent.

In a second experiment, the conditions were altered by using a larger excess of Grignard's reagent, to which the ethereal solution of the ester was added. Five grams of menthyl benzoylformate (1 mol.) dissolved in 40 c.c. of ether were added within an interval of 10 minutes to magnesium ethyl bromide (3 mols.) dissolved in 40 c.c. of ether. The action was moderated by immersion of the flask, containing the reaction mixture, in ice-cold water. After 12 hours at the temperature of the laboratory, the mixture was heated to gentle boiling for 2 hours and then cooled and decomposed carefully by water and dilute hydrochloric acid. The product obtained was hydrolysed as before. The aqueous solution of potassium salt, obtained after complete removal of the menthol formed from the hydrolysis, was decolorised by animal charcoal, and, when examined in a 2 dcm. tube, gave  $\alpha_D^{16^\circ} - 1^\circ$ , whilst the zinc salt prepared from the acid was also distinctly lævorotatory.

In a third experiment, where the same amounts of menthyl benzoylformate and magnesium ethyl bromide as in the second experiment

were used, the ethereal solution of the ester was added in one instalment to Grignard's reagent. After the vigorous action had subsided, the mixture was heated on the water-bath for  $1\frac{1}{2}$  hours. The hydrolysis was conducted as previously described. The aqueous solution of potassium salt, obtained after removal of the menthol, was heated with animal charcoal and then gave  $\alpha_D^{16} - 0.80^\circ$  ( $l=2$ ); the alcoholic solution of the acid obtained from it gave  $\alpha_D^{18} - 0.41^\circ$  ( $l=0.5$ ). The silver salt of the acid was analysed:

0.4485 gave 0.1701 Ag.  $\text{Ag} = 37.9$ .

$\text{C}_{10}\text{H}_{11}\text{O}_3\text{Ag}$  requires  $\text{Ag} = 37.6$  per cent.

*Action of Magnesium Methyl Iodide on Menthyl Benzoylformate.*

Magnesium (1.26 grams = 3 mols.) was added to a solution of 7.4 grams of methyl iodide (3 mols.) in 30 c.c. of anhydrous ether. When the magnesium had practically all dissolved, the solution was cooled in ice-cold water and a solution of 5 grams of menthyl benzoylformate (1 mol.) in 30 c.c. of ether added to it in one instalment. The solution instantly turned dark brown from the separation of iodine, but there was no ebullition until the flask was shaken, when the reaction proceeded with violence, the solution becoming almost colourless and a solid product separating. After the mixture had been boiled gently for  $1\frac{1}{2}$  hours, ice was gradually added and then an excess of dilute hydrochloric acid. The ethereal layer was separated and the residue extracted with ether. The total ethereal solution was then agitated with a little dilute sulphurous acid to remove the free iodine present in small amount and then washed with water. The oil, obtained after removal of the ether, was then heated with 33 c.c. of ethyl alcohol and 17 c.c. of alcoholic potassium hydroxide (1 c.c. = 0.0606 gram KOH) for one hour, after which the ethyl alcohol was evaporated off and water added to the resulting oil. The solid menthol was next drained off and the alkaline filtrate heated on a boiling water-bath with animal charcoal for several hours, by which time all the menthol had been expelled. When the filtered solution was extracted with ether, 0.15 gram of a substance was obtained, melting indistinctly between  $65^\circ$  and  $70^\circ$  and yielding an optically inactive solution when dissolved in ethyl alcohol. This substance, which may possibly have been the ditertiary glycol,  $\text{CMePh(OH)} \cdot \text{CMe}_2(\text{OH})$ , formed owing to the presence of the excess of Grignard's reagent in the initial action, was not further examined. The solution from which it had been removed was next neutralised by the addition of a few drops of dilute hydrochloric acid. The volume measured 16 c.c., and 14 c.c. of this, when examined in a 2 dm. tube, had the

rotation  $\alpha_D^{17} - 4.16^\circ$ ; the solution, when extracted with ether six times, did not alter in rotation and the ethereal extract yielded the merest trace of a residue. In this way, it was conclusively proved that the activity observed could not have been due to the above-mentioned by-product.

When an excess of hydrochloric acid was added to the solution of potassium salt, a solid separated. This is in accordance with the properties of phenylmethylglycollic acid, which can be recrystallised from water (Fittig and Wurster, *Annalen*, 1879, 195, 153; Fittig and Kast, *Annalen*, 1880, 206, 24). The acid was quantitatively extracted with ether, and the liquid, which had been extracted, when tested in the polarimeter, was inactive. The acid, obtained after removal of the ether, was a white solid, which, when dried in a vacuum over sulphuric acid, softened at  $84^\circ$  and melted completely at  $88^\circ$ : 2.2676 grams were obtained, and a determination of its specific rotation in ethyl alcohol gave the following result:

$$l = 4, c = 9.0704, \alpha_D^{18} - 3.44^\circ, [\alpha]_D^{18} - 9.5^\circ.$$

The product seemed to be a mixture of *i*- and *l*-phenylmethylglycollic acids. The melting point of the former acid,  $93-94^\circ$ , is apparently lowered by the presence of the active isomeride, the amount of which present in the mixture cannot yet be determined as the optically active form has so far not been described. When the mixture was crystallised from light petroleum, the crop which separated melted at  $90-91.5^\circ$  and had  $[\alpha]_D - 11.6^\circ$  ( $c = 2.669$ ) in ethyl-alcoholic solution.

In a second experiment, Grignard's reagent, prepared from 0.42 gram of magnesium (1 mol.) and 2.5 grams of methyl iodide (1 mol.) and 40 c.c. of ether, was added drop by drop to a solution of 5 grams of menthyl benzoylformate (1 mol.) in 20 c.c. of ether. As soon as the magnesium methyl iodide had been prepared, the flask containing it was quickly connected with the flask containing the ester by means of a doubly-bored stopper, through one hole of which passed a siphon provided with a stop-cock, whilst the other hole was fitted with a U-tube filled with solid potassium hydroxide. The flask containing the ester was in turn attached to a reflux condenser provided with a guard-tube of calcium chloride and soda-lime. By this arrangement, the addition of the magnesium methyl iodide could be conveniently regulated; it was added drop by drop within an interval of 45 minutes. The solution of the ester became dark brown as soon as the magnesium methyl iodide was added; this coloration persisted, and towards the end of the reaction a solid crystalline compound separated. The ether boiled gently towards the end of the reaction, which never at any time became vigorous. After

12 hours, ice and dilute hydrochloric acid were added successively, after which the ethereal layer was separated, washed with sulphurous acid and then with water. The ether was expelled, and the resulting oil boiled with 50 c.c. of ethyl alcohol and 17 c.c. of alcoholic potassium hydroxide (1 c.c. = 0.0606 gram KOH) for one hour. The menthol was removed, and the potassium salt remaining was extracted with ether, when it was found that in this case the ethereal solution left no residue. The solution was decolorised with animal charcoal and, when filtered and evaporated to 14 c.c., the bulk necessary to fill the 2-dcm. tube used, gave  $\alpha_D^{20} = 4.51^\circ$ . The acid, obtained as before, had  $[\alpha]_D^{20} = 8.3^\circ$  ( $c = 6.718$ ) in ethyl-alcoholic solution, this determination having been made with a specimen which had been fused by heating on a boiling water-bath and then dried in a vacuum over sulphuric acid.

0.1904 gave 0.1096  $H_2O$  and 0.4536  $CO_2$ .  $H = 6.4$ ;  $C = 65.0$ .

$C_9H_{10}O_3$  requires  $H = 6.0$ ;  $C = 65.1$  per cent.

*Action of Magnesium Phenyl Bromide on Menthyl Benzoylformate.*

Magnesium (1.26 grams = 3 mols.) was added to a solution of 8.1 grams of bromobenzene (3 mols.) in 40 c.c. of ether. When the mixture was warmed, the action started, and when it was complete the solution was gradually added within an interval of 7 minutes to a solution of 5 grams of menthyl benzoylformate (1 mol.) in 40 c.c. of ether, the action being moderated by cooling in ice. After being boiled for two hours, the product was decomposed by ice and hydrochloric acid, the ester obtained hydrolysed as usual, and the menthol removed. The aqueous solution of potassium salt was concentrated by evaporation and a crop allowed to crystallise. After removal of this, the filtrate was heated with animal charcoal. When the latter was separated, the solution was examined in the polarimeter and proved to be inactive. When acidified by hydrochloric acid, a solid separated, which, when recrystallised from water, separated in needles, melted at  $149-150^\circ$ , and had the properties of benzilic acid. Its solution in concentrated sulphuric acid was carmine-red. Its silver salt was analysed:

0.5748 gave 0.1853 Ag.  $Ag = 32.2$  per cent., being the amount calculated for  $C_{14}H_{11}O_3Ag$ .

The crop, which had been removed from the solution of potassium salt, proved to be potassium benzilate. Its aqueous solution was inactive, and, when acidified, yielded benzilic acid, which was identified by its melting point and its colour reaction with concentrated sulphuric acid.

In a second experiment, a solution of 0.42 gram of magnesium (1 mol.) in 2.7 grams of bromobenzene (1 mol.) and 40 c.c. of ether was added drop by drop to a solution of 5 grams of menthyl benzoylformate (1 mol.) in 20 c.c. of ether. The operations were conducted so far as possible under the same conditions as those already described for the second experiment on the action of magnesium methyl iodide on menthyl benzoylformate. The aqueous solution of potassium salt, obtained after removal of the menthol, was quite inactive, and, when acidified, yielded benzoic acid.

The applicability of Grignard's reaction for the asymmetric syntheses of other acids from the menthyl and bornyl esters of ketonic acids is at present under investigation.

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### CXXVIII.—*The Relation of Position Isomerism to Optical Activity. II. The Rotation of the Menthyl Esters of the Isomeric Chlorobromobenzoic Acids.*

By JULIUS BEREND COHEN and HENRY STANLEY RAPER.

IN continuation of the research begun by Briggs and Cohen on the relation of position isomerism to the activity of the menthyl esters of the six isomeric dichlorobenzoic acids (Trans., 1903, 83, 1213), we have now prepared and examined the menthyl esters of the ten isomeric chlorobromobenzoic acids.

These esters were obtained in most cases by the method employed in the preparation of the chlorobenzoic esters, namely, by oxidising the corresponding chlorobromotoluenes to the acids, converting the acids into the acid chlorides, and, finally, preparing the esters by heating the acid chlorides with menthol.

The following tables contain some of the physical constants of the acids (only four of them had been previously obtained in a more or less impure state), the acid chlorides, and the menthyl esters. Details of their preparation are given in the experimental part which follows.

TABLE I.

Chlorobromo- benzoic acid.		M. p.	M. p. of corre- sponding di- chlorobenzoic acid.	Chlorobromo- benzoic acid.		M. p.	M. p. of corre- sponding di- chlorobenzoic acid.
Cl	Br			Cl	Br		
2 : 3		165°	163°	2 : 5		155—6°	153°
3 : 2		143—4		5 : 2		148—9	
2 : 4		166—7	160	3 : 4		218	200—201
4 : 2		154—5		4 : 3		214	
2 : 6		143—4	139—140	3 : 5		189—190	182—183

The effect of interchanging the two halogens is very marked. When the chlorine occupies a position nearer to the carboxyl than the bromine, the melting point is higher than in the reverse positions. The melting point is highest where both halogens are farthest from the carboxyl (3 : 4) and lowest when they are nearest to the carboxyl (2 : 6). It is remarkable that the menthyl ester (see below) should show the very reverse of this, the 2 : 6 ester having a peculiarly high melting point.

TABLE II.

Chlorobromo- benzoyl chloride.		M. p.	B. p.	Pres- sure in mm.	Chlorobromo- benzoyl chloride.		M. p.	B. p.	Pres- sure in mm.
Cl	Br				Cl	Br			
2 : 3		41—42°	150—152°	25	2 : 5		—	147°	19
3 : 2		40—41	144—146	22	5 : 2		34—35°	146—147	23
2 : 4		35—36	152—153	22	3 : 4		58—59	not distilled	—
4 : 2		32—33	155—156	29	4 : 3		37—38	not distilled	—
2 : 6		30	145—147	24	3 : 5		33—34	149—151	19

Table III (p. 1264) gives the melting points, boiling points, densities, specific and molecular rotations of the series of menthyl esters, together with the corresponding constant for menthyl benzoate and the menthyl esters of the dichlorobenzoic acids.

The table on p. 1264 confirms in a very satisfactory way the results obtained with the series of dichlorobenzoic esters. It will be observed that the greatest effect in decreasing the rotation is produced when the halogen enters the ortho-position with respect to the ester radicle, the least when both halogens are in the meta-position; from which it

TABLE III.

Menthyl ester of chloro- bromobenzoic acid.	M. p.	B. p.	Pres- sure in mm.	Density at 20°.	$[\alpha]_D^{20^\circ}$ .	$[M]_D^{20^\circ}$ .	$[M]_D^{20^\circ}$ of the corre- sponding menthyl dichloro- benzoate.
Cl Br							
2 : 3	31—32°	237—239°	22	1.2582	-46.18°	-172.5°	} -172.9°
3 : 2	—	227—229	14	1.2372	-51.82	-193.5	
2 : 4	—	224—226	18	1.2683	-54.57	-203.9	
4 : 2	—	221—223	18	1.2723	-53.70	-219.2	} -209.6
2 : 5	34—35	224	20	1.2764	-50.91	-190.2	
5 : 2	36.5—37.5	221—222	17	1.2677	-55.68	-207.8	} -199.4
				In ben- zene *			
2 : 6	144—145	not distilled	—	solution.	-8.70	-32.5	-113
3 : 4	46—47	225—227	18	1.2866	-55.67	-207.9	} -227.5
4 : 3	35—36	223—225	10	1.2854	-59.15	-220.9	
3 : 5	—	226—228	21	1.2444	-62.90	-235.9	
Menthyl benzoate (Tschugaeff)	} 54	—	—	In ben- zene solution.	-90.92	-236.3	-233.2

\* Owing to its high melting point, the rotation of the 2:6-chlorobromobenzoic ester could not be determined in the pure state; it was therefore observed in benzene solution, and the rotation of the pure substance obtained by extrapolation, see p. 1268.

would follow that the para-halogen occupies an intermediate position.

The order of magnitude, beginning with the ester of lowest rotation, is roughly as follows:

2:6; 2:3; 2:5; 2:4; 3:4; 3:5; phenyl;

which is precisely the order of rotation of the dichloro-esters (*loc. cit.*, p. 1215).

A further interesting relation is brought out by a comparison of the pairs of esters with reversed positions of the halogens. When the chlorine is nearer to the ester group than the bromine, a greater depression in the rotation is produced than in the reverse arrangement. Moreover, where the chlorine occupies the ortho-position to the ester group, the rotation is lower than that of the corresponding dichloro-ester. The general effect of bromine is to lower the rotation less than the chlorine—a result which might have been anticipated from a comparison of the monohalogen esters (*loc. cit.*, p. 1216). This effect is perhaps most obvious in the 3:5-chlorobromo-ester, which produces less effect on the rotation than the corresponding 3:5-dichloro-com-

pound. It is, in fact, almost identical with the unsubstituted menthyl ester.

The great contrast afforded by the two symmetrical compounds of both series, namely, 3 : 5- and 2 : 6-esters (which naturally have only one representative each), is not a little remarkable. They may be regarded as the first and last terms of a series. The 2 : 6-compounds possess a high melting point and low rotation; the 3 : 5-compounds a low melting point, low density, and high rotation. Is there any direct and simple connection between these physical properties? This is a question we shall not attempt at present to answer. We hope by extending this field of inquiry and by collecting further material to obtain more definite views on these points.

### EXPERIMENTAL.

#### *Preparation of the Chlorobromobenzoic Acid, Acid Chlorides, and Menthyl Esters.*

The general method for preparing the acids was to heat in sealed tubes the corresponding chlorobromotoluenes with 4 parts of dilute nitric acid (1 part of nitric acid of sp. gr. 1.4 to 2 parts of water) at 130° for one hour and then at 135° for two to three hours. The acid chlorides were obtained by heating the acid with phosphorus pentachloride at 130—140° in the oil-bath for half an hour. The oxychloride was then removed by distillation on the water-bath under reduced pressure and the acid chloride further purified by distillation also under reduced pressure. The menthyl esters were prepared by heating the acid chloride with the calculated quantity of menthol at 140° until hydrogen chloride ceased to be evolved. It may be observed that the 2 : 6-chlorobromobenzoyl chloride, like the corresponding dichlorobenzoyl chloride, does not react with menthol until a temperature of 180° is reached. The product was made slightly alkaline with sodium carbonate and any unaltered menthol or menthyl chloride removed by distillation in steam. The ester which remained in the distilling flask was then extracted with ether, the ethereal solution dehydrated, and the solvent removed first on the water-bath and finally *in vacuo*. The rotation was then observed, after which the ester was distilled under diminished pressure and a second observation made. As in the case of the dichlorobenzoic esters, a small quantity of solid appeared in the distillate from some of the esters, which was found to be the free acid, but the decomposition was very slight and the rotation, after removal of the acid, was unaffected. Except in the case of the 5-chloro-2-bromo- and 3-chloro-4-bromo-compounds, the rotation of the esters before distillation was slightly higher than the rotation after

the ester had been distilled. The rotation was determined in a 0.302 decimetre jacketed metal tube which was made specially for us by Schmidt and Haensch. The jacket was furnished with an inlet and outlet tube like a small condenser, so that a current of water or vapour at constant temperature could be passed through the apparatus whilst the observations were being made. In the present case, the same temperature (20°) was employed. The polarimeter made by Schmidt and Haensch could be read to 0.01°.

*2-Chloro-3-bromobenzoic Acid.*—The starting point for the preparation of the acid was 3-nitro-*o*-toluidine, obtained by the nitration of aceto-*o*-toluidide (Reverdin and Crépieux, *Ber.*, 1900, 33, 2498). The amino-group was replaced by chlorine, the chloronitrotoluene reduced with tin and hydrochloric acid, and the resulting chlorotoluidine dissolved in the calculated quantity of hydrochloric acid and diazotised. The diazo-chloride was then added to cuprous bromide to which sufficient hydrobromic acid (sp. gr. 1.5) was added to give a clear solution and the resulting chlorobromotoluene separated by distillation in steam. It was further purified by distillation under reduced pressure. The portion boiling at 125—135° under 50 mm. pressure was collected. Thirty grams of chlorotoluidine gave 20 grams of chlorobromotoluene. The chlorobromotoluene was oxidised with dilute nitric acid in the manner already described, and the acid purified by recrystallisation from alcohol, in which it is very soluble. Fourteen grams of the chlorobromo-compound gave 9 grams of acid melting at 165°.

The analyses of the acids and esters are arranged in Tables IV and V at the end of the paper. The properties of the acid chloride and menthyl ester have already been given in the previous tables.

*3-Chloro-2-bromobenzoic Acid.*—The chlorobromotoluene required for this preparation was obtained from 3-nitro-*o*-toluidine by a similar series of reactions to those described above. Sixty grams of the nitrotoluidine yielded 20 grams of 3-chloro-2-bromotoluene boiling at 103—105° under 25 mm. pressure. The compound was oxidised in the usual way with nitric acid and converted into the acid. The product is difficult to purify owing to the formation of a small quantity of a second acid, melting at 233—235°, and crystallising in well-defined prisms from alcohol; this substance was not further investigated. The two compounds may be separated by means of ligroin, in which the 3-chloro-2-bromobenzoic acid is much more soluble. The acid was further purified by several crystallisations from benzene and then melted at 143—144°. Fourteen grams of 3-chloro-2-bromotoluene yielded not more than 3 grams of the pure acid.

*2-Chloro-4-bromobenzoic Acid.*—Willgerodt and Salzmann (*J. pr. Chem.*, 1889, [ii], 39, 470) first prepared the acid from 2-chloro-4-bromo-

toluene, which they obtained by chlorinating *p*-bromotoluene. They give 156° as the melting point. We obtained the chlorobromotoluene from 2:4-nitrotoluidine by the usual series of operations. It boiled at 100—110° under 10 mm. pressure. The acid obtained by oxidation was purified by recrystallisation from alcohol, in which it is moderately soluble. Fourteen grams of chlorobromotoluene gave 10 grams of the acid, which crystallises in colourless needles melting at 166—167°. The acid obtained by Willgerodt and Salzmänn was evidently impure.

*4-Chloro-2-bromobenzoic Acid.*—This acid was also described by Willgerodt and Salzmänn (*loc. cit.*). The bromochlorotoluene which served for the preparation was obtained by the chlorination of *o*-bromotoluene or the bromination of *p*-chlorotoluene, and the acid is described as melting at 217°, which is clearly incorrect. Our acid was obtained from 2:4-nitrotoluidine in the manner previously described. Fifty grams of the base gave 20 grams of the chlorobromotoluene, boiling at 112—114° under 12 mm. pressure. Fourteen grams were oxidised and the acid recrystallised from alcohol; it crystallises in colourless needles which melt at 154—155°.

*2-Chloro-5-bromobenzoic Acid.*—The 2-chloro-5-bromotoluene was prepared in the usual way from 5-nitro-*o*-toluidine. Thirty grams of nitrotoluidine yielded 14 grams of 2-chloro-5-bromotoluene boiling at 127—129° under 45 mm. pressure. The acid obtained on oxidation was purified by crystallisation from glacial acetic acid. The acid is very soluble in alcohol and melts at 155—156°.

*5-Chloro-2-bromobenzoic Acid.*—The acid was prepared by two methods. (1) The 5-chloro-2-bromotoluene required for oxidation was obtained from 5-chloroaceto-*o*-toluidide, which, in turn, was prepared by the action of sodium hypochlorite on aceto-*o*-toluidide (Chattaway and Orton, *Trans.*, 1900, 77, 790). The 5-chloroaceto-*o*-toluidide was hydrolysed by boiling for an hour with about four times its weight of concentrated hydrochloric acid. The solution was neutralised with sodium carbonate and the chlorotoluidine separated by distillation in steam. The amino-group was then replaced by bromine. The 5-chloro-2-bromotoluene obtained in this way boiled at 98—100° under 25 mm. pressure. The 5-chloro-2-bromobenzoic acid, prepared by oxidation, was purified by recrystallisation from benzene and melted at 148—149°. The acid is very soluble in alcohol.

(2) 5-Chloro-2-nitrobenzoic acid, obtained by Hübner's method (*Annalen*, 1884, 222, 95), was reduced to the amino-compound and converted by Sandmeyer's reaction into the corresponding chlorobromobenzoic acid. The acid prepared by this method had the same melting point as the one obtained by the previous process, but it was slightly discoloured.

*2-Chloro-6-bromobenzoic Acid.*—The acid has been described by Willgerodt and Salzmann (*J. pr. Chem.*, 1889, [ii], 39, 473), who obtained it by the oxidation of 2-chloro-6-bromotoluene. They give the melting point as  $132^{\circ}$  instead of  $143\text{--}144^{\circ}$ , and, as in other cases referred to, the compound is evidently impure.

We prepared the acid from 2:6-dinitrotoluene, which was converted by the usual series of reactions into 2-chloro-6-bromotoluene. The latter was purified by distillation under reduced pressure. Fifty-six grams of 2-chloro-6-nitrotoluene gave 27 grams of chlorobromotoluene boiling at  $118\text{--}120^{\circ}$  under 40 mm. pressure.

The acid, obtained by oxidation, was purified by crystallisation from ligroin mixed with about 20 per cent. of benzene. It crystallises in needles which are very soluble in alcohol and melt at  $143\text{--}144^{\circ}$ . Twenty grams of chlorobromotoluene yielded 12 grams of the pure acid. This product was converted into the acid chloride and menthyl ester in the usual way. We have already pointed out the difficulty with which the acid chloride reacts with menthol, resembling in this respect the corresponding dichlorobenzoyl chloride. They furnish interesting examples of steric hindrance.

As the menthyl ester has a high melting point, it was necessary to determine the rotation in solution. The following are the specific rotations of different concentrations in benzene solution:

Concentration per cent.	$[\alpha]_D^{20^{\circ}}$ .
6.57	$-8.07^{\circ}$
13.15	$-8.67$
17.91	$-8.69$
22.79	$-8.72$
28.24	$-8.68$

It will be seen that at the higher concentrations the rotation curve is a straight line. The last three observations are identical within the error of experiment. The mean  $-8.70^{\circ}$  gives a molecular rotation of  $-32.5^{\circ}$ . At a temperature of  $55^{\circ}$ , a 42.51 per cent. solution gives  $[\alpha]_D^{55^{\circ}} = -15.97^{\circ}$ , which, by analogy, is the number one would anticipate at that temperature. In order to find whether the benzene produced an abnormal rotation, solutions of the 5-chloro-2-bromobenzoic ester in benzene were prepared and examined in the polarimeter with the following result:

Concentration per cent.	$[\alpha]_D^{20^{\circ}}$ .
21.30	$-57.51^{\circ}$
30.21	$-57.66$

The specific rotation of the liquid ester at  $20^{\circ}$  is  $-55.68^{\circ}$ . The slight difference between the rotation in solution and in the fused state may

be accounted for by the fact that the ester from which the solutions were prepared had crystallised since the first determination was made, when it was still in a fluid condition. As the crystals had been pressed on a porous plate, it is possible that the crystallised specimen was rather purer than the original substance. The result is, in any case, sufficient to show conclusively that the specific rotation in solution at moderate concentrations is essentially the same as that of the fused substance.

*3-Chloro-4-bromobenzoic Acid.*—The acid is described by Willgerodt and Salzmänn (loc. cit.), who obtained it by the oxidation of the corresponding toluene derivative, which in turn was prepared by chlorinating *p*-bromotoluene. The melting point,  $170^{\circ}$ , which they give shows that the substance was not pure.

The starting point for the preparation of the acid was *m*-chloro-*p*-toluidine prepared by Cohen and Dakin's method (Trans., 1902, 81, 1324). The amino-group was replaced by bromine in the usual way and the chlorobromotoluene purified by distillation under reduced pressure. It boils at  $125\text{--}130^{\circ}/25$  mm. Thirty-three grams of the chlorotoluidine gave 27 grams of 3-chloro-4-bromotoluene. The latter was oxidised and the product crystallised from alcohol. From 17 grams of chlorobromotoluene, 12 grams of acid melting at  $218^{\circ}$  were obtained.

*4-Chloro-3-bromobenzoic Acid.*—The acid was prepared from *m*-nitro-*p*-toluidine. The 4-chloro-3-bromotoluene boils at  $120\text{--}125^{\circ}/28$  mm. Fifty grains of the original base gave 12 grams of the toluene derivative, from which the acid was obtained by oxidation. After recrystallisation from alcohol, in which it is moderately soluble, the acid melted at  $214^{\circ}$ .

*3-Chloro-5-bromobenzoic Acid.*—The acid was obtained by two methods.

(1) The starting point was 5-nitro-*o*-toluidine, which was brominated in acetic acid solution instead of in aqueous solution, as directed by Nevile and Winther (Trans., 1880, 37, 429). By the use of acetic acid, the reaction is much more rapid and the product comparatively pure. The 3-bromo-5-nitro-2-toluidine was purified from glacial acetic acid. The amino-group was then removed by diazotising in alcoholic solution and the bromonitrotoluene distilled off in steam. The nitro-group was replaced by chlorine and the resulting chlorobromotoluene distilled in steam and purified by crystallisation from alcohol. It melts at  $25\text{--}26^{\circ}$ . Sixty-four grams of bromonitrotoluidine gave 7 grams of chlorobromotoluene.

(2) Aceto-*p*-toluidide dissolved in acetic acid was brominated by adding the calculated quantity of bromine, allowing the mixture to remain for an hour, and pouring into water. Five parts of the *m*-bromoaceto-

*p*-toluidide prepared in this way were dissolved in five times the weight of a mixture of equal volumes of concentrated hydrochloric acid and glacial acetic acid. The solution was cooled to 10° and kept at this temperature, whilst a solution of 1 part of sodium chlorate in 5 parts of water was added. After a time, the chlorobromoacetotoluidide which had separated was filtered and purified by crystallisation from alcohol, when it melted at 201—202°.

0.1307 gave 0.1626 AgCl + AgBr.

$C_9H_9NClBr$  requires 0.1650 AgCl + AgBr.

The chlorobromoacetotoluidide was hydrolysed by heating in a sealed tube with strong hydrochloric acid at 120° for an hour. The amino-group was removed by diazotising in alcohol and the chlorobromotoluene distilled off in steam; it melted at 25—26° after crystallisation. Seventeen grams of chlorobromoacetotoluidide gave 7 grams of pure 3:5-chlorobromotoluene.

The chlorobromotoluene (17 grams) yielded on oxidation the acid (9.5 grams), which, after crystallisation from benzene containing a little alcohol, melted at 189—190°.

TABLE IV.

*Analyses of the Chlorobromobenzoic Acids.*

Chlorobromobenzoic Acid. Cl Br	Substance taken.	AgCl + AgBr found.	AgCl + AgBr calculated.
2 : 3	0.1478	0.2111	0.2080
3 : 2	0.1086	0.1567	0.1529
2 : 4	0.1482	0.2079	0.2085
4 : 2	0.1589	0.2211	0.2236
2 : 5	0.1421	0.2000	0.2000
5 : 2	0.1641	0.2318	0.2310
2 : 6	0.1977	0.2803	0.2785
3 : 4	0.1506	0.2107	0.2119
4 : 3	0.1760	0.2467	0.2476
3 : 5	0.1441	0.2054	0.2028

TABLE V.

*Analyses of the Chlorobromobenzoic Esters.*

Menthyl Ester.		Substance taken.	AgCl + AgBr found.	AgCl + AgBr calculated.
Cl	Br			
2	3	0.2798	0.2496	0.2483
3	2	0.1386	0.1182	0.1230
2	4	0.1848	0.1595	0.1640
4	2	0.1553	0.1353	0.1378
2	5	0.1470	0.1291	0.1304
5	2	0.2966	0.2594	0.2632
2	6	0.1574	0.1405	0.1397
3	4	0.1546	0.1372	0.1372
4	3	0.1952	0.1731	0.1732
3	5	0.1721	0.1540	0.1527

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CXXIX.—*The Relation of Position Isomerism to Optical Activity. III. The Rotation of the Menthyl Esters of the Isomeric Iodobenzoic Acids.*

By JULIUS BEREND COHEN and HENRY STANLEY RAPER.

IN a former communication (Cohen and Briggs, *Trans.*, 1903, 83, 1216), the rotations of the menthyl esters of the three monochlorobenzoic acids were given and compared with the constants obtained by Tschugaeff (*Abstr.*, 1903, 84, ii, 2) for the three monobromobenzoic esters. It seemed desirable to complete the series by determining the constants of the esters of the three iodobenzoic acids, which has now been done with the results on p. 1272.

The results are somewhat remarkable. The rotation of the ester of *o*-iodobenzoic acid rises suddenly above that of the *o*-bromo-ester; the *m*-ester sinks slightly below that of the other two meta-compounds, whilst the para-ester shows the same gradual rise which differentiates the bromo- from the chloro-ester. But, whereas the meta- and para-esters exhibit among themselves differences not exceeding 4° and not above 5° between them and menthyl benzoate, the ortho-esters differ among themselves by more than 50°. If we compare the members of the ortho-series with one another and with menthyl benzoate, we see

*Molecular Rotations of the Menthyl Esters of the Chloro-, Bromo-, and Iodo-benzoic Acids.*

Menthyl benzoate  $[\text{M}]_D^{20} = 236.3^\circ$  (Tschugaeff).

Menthyl chlorobenzoate (C. and B.).	$[\text{M}]_D^{20}$ .	Menthyl bromobenzoate (Tschugaeff).	$[\text{M}]_D^{20}$ .	Menthyl iodobenzoate (C. and R.).	$[\text{M}]_D^{20}$ .
ortho	-195.0°	ortho	-205.3°	ortho	-246°
meta	-236.9	meta	-238.7	meta	-234.5
para	-237.3	para	-238.8	para	-241.2

that the rotations vary on each side of the value for menthyl benzoate. If the effect of the three halogens on the ester group were the same in character but different in magnitude, we should expect a change—it might be gradual or abrupt—but a change in one direction.

This is not the case, and we are therefore compelled to recognise at least two factors simultaneously affecting rotation, namely, the chemical nature of the non-active group and its position in regard to the active group, which may act together or in opposite directions in increasing or diminishing the rotation of the active group.

#### EXPERIMENTAL.

*o*-Iodobenzoic acid was prepared from anthranilic acid by replacing the amino-group by iodine in the usual way. The acid was separated by filtration and crystallised from dilute acetic acid. Anthranilic acid gave about an equal weight of *o*-iodobenzoic acid melting at 162°. Prepared in this manner, the acid has a brown colour, which it does not lose on repeated crystallisation. In order to purify it, it was converted into the ethyl ester by Fischer and Speier's method, and then distilled under reduced pressure. Sixteen grams of the discoloured acid gave 13 grams of ethyl ester (b. p. 163–165°/23 mm.)

The ester was hydrolysed by heating it on the water-bath with the calculated quantity of methyl-alcoholic potash. It was then dissolved in water, acidified, and filtered. It now melted at 162–163° and was perfectly colourless.

*o*-Iodobenzoyl Chloride.—The acid chloride was prepared by heating equal weights of acid and phosphorus pentachloride at 130–135° in the oil-bath for half an hour. The phosphorus oxychloride was removed on the water-bath by distillation under diminished pressure, and the acid chloride was then distilled. It boils at 159°/27 mm., and solidifies on cooling; the melting point is 30–31°.

*Menthyl o*-Iodobenzoate.—The ester was prepared by heating the

acid chloride with an equal weight of menthol to 130—140° in the oil-bath until the evolution of hydrochloric acid ceased. The product was made slightly alkaline with sodium carbonate and the menthol removed by distillation in steam. The ester which remained in the distilling vessel was extracted with ether, dehydrated, and the ether removed by distillation, and finally by heating on the water-bath under reduced pressure. Ten grams of acid chloride gave 11 grams of ester. It is a colourless, viscid liquid, which decomposes on distillation even under reduced pressure.

0.1547 gave 0.0948 AgI.  $I = 33.1$ .

$C_{17}H_{23}O_2I$  requires  $I = 32.9$  per cent.

The rotation observed in a 0.302 decimetre tube at 20° gave  $-26.46^\circ$ ; sp. gr. 1.375 at 20°.

$$[\alpha]_D^{20^\circ} - 63.72^\circ; [M]_D^{20^\circ} - 246^\circ.$$

*m-Iodobenzoic Acid*.—The acid was prepared from *m*-aminobenzoic acid in precisely the same manner as the ortho-compound, and, like the ortho-compound, it was discoloured. It was purified in the same manner, by conversion into the ethyl ester and distilling under reduced pressure. The ethyl ester boils at 165—166°/24 mm.; it was hydrolysed with alcoholic potash, and the acid, when precipitated with hydrochloric acid, was recrystallised from acetone and melted at 187—188°.

*m-Iodobenzoyl chloride* was prepared like the ortho-compound and purified by distillation under reduced pressure; it boils at 159—160°/23 mm., and is liquid at the ordinary temperature.

*Menthyl m-iodobenzoate* was obtained by heating the acid chloride with menthol, as described under the ortho-compound, and purified in the same manner. The acid chloride gave nearly an equal weight of menthyl ester in the form of a viscid liquid, which had a pale amber colour, owing, no doubt, to some slight impurity.

0.1530 gave 0.0935 AgI.  $I = 33.0$ .

$C_{17}H_{23}O_2I$  requires  $I = 32.9$  per cent.

The rotation in a 0.302 decimetre tube at 20° gave  $-24.95^\circ$ ; sp. gr. 1.360 at 20°.

$$[\alpha]_D^{20^\circ} - 60.75^\circ; [M]_D^{20^\circ} - 234.5^\circ.$$

*p-Iodobenzoic Acid*.—The acid was prepared by oxidising *p*-iodotoluene in sealed tubes with dilute nitric acid at 135° for 3 hours. Some iodine was liberated. The acid was filtered off and the free iodine removed with sodium hydrogen sulphite solution. The product was then dissolved in sodium carbonate solution, filtered from any unchanged *p*-iodotoluene, and acidified; the acid was collected and

crystallised from alcohol or acetic acid. Sixteen grams of iodotoluene yielded 11 grams of pure acid melting at  $265^{\circ}$ .

*p*-Iodobenzoyl chloride was obtained by the method already described, and purified by distillation under reduced pressure. The acid chloride boiled at  $163\text{--}164^{\circ}/32$  mm.; on cooling, it solidified and melted at  $71\cdot2^{\circ}$ .

*Menthyl p*-iodobenzoate was prepared in the ordinary manner. Nine grams of acid chloride yielded 10 grams of ester. This ester, like the two previously described, is a viscid liquid at the ordinary temperature.

0.1301 gave 0.0644 AgI.  $I = 33\cdot6$ .

$C_{17}H_{23}O_2I$  requires  $I = 32\cdot9$  per cent.

The rotation in a 0.302 decimetre tube at  $20^{\circ} = -24\cdot74^{\circ}$ ; sp. gr. = 1.311.

$[\alpha]_D^{20} = -62\cdot48^{\circ}$ ;  $[M]_D^{20} = -241\cdot2^{\circ}$ .

The following table gives a summary of the constants of the compounds described above.

	Iodobenzoic acid, m. p.	Iodobenzoyl chloride.			Menthyl iodobenzoate.	$\Delta^{20^{\circ}}$ .
		B. p.	Pressure.	M. p.		
ortho	$162^{\circ}$	$159^{\circ}$	27 mm.	$30\text{--}31^{\circ}$	viscid liquid	1.375
meta	$187\text{--}188$	$159\text{--}160$	23 "	—	"	1.360
para	265	$163\text{--}164$	32 "	$71\text{--}72$	"	1.311

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### CXXX.—*The Chlorination of the Trichlorotoluenes in Presence of the Aluminium-mercury Couple. The Constitution of the Tetrachlorotoluenes. Part V.*

By JULIUS BEREND COHEN and HENRY DRYSDALE DAKIN.

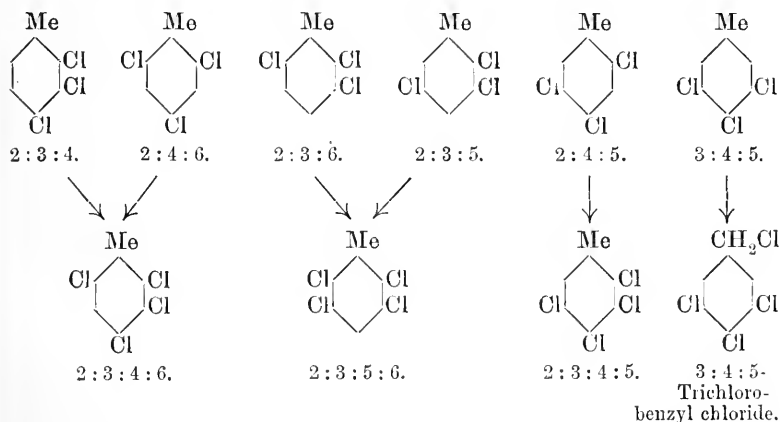
IN our previous papers (Part III, Trans., 1901, 79, 1111; Part IV, Trans., 1902, 81, 1325), the progressive chlorination of toluene has been traced as far as the formation of the trichlorotoluenes. We have now carried the investigation a step further, and determined the character of the products formed by introducing a fourth chlorine atom into each of the six trichlorotoluenes.

This stage of the investigation has been simplified, inasmuch as there are only three tetrachlorotoluenes into which the six trichloro-

toluenes could be converted, and of the latter the two symmetrical compounds, namely, the 2:4:6- and 3:4:5-isomerides, can theoretically only yield one product each, provided the chlorine atom enters the nucleus.

But, as the nucleus becomes loaded with chlorine, it is conceivable that steric hindrance might determine the entrance of the halogen into the side-chain, and we have strong evidence that this occurs with 3:4:5-trichlorotoluene. On chlorinating this compound at 0° in presence of the couple, a tetrachloro-compound is formed, which is quite distinct from 2:3:4:5-tetrachlorotoluene and gives a different nitro-derivative. The only explanation of this fact is that the fourth chlorine atom enters the methyl group and not the nucleus. The phenomenon, as far as we know, is quite unique, and leads us to anticipate the possibility of a similar behaviour on the part of the tetrachlorotoluenes when the fifth chlorine atom is introduced in the final stage of chlorination, an investigation upon which we are now engaged.

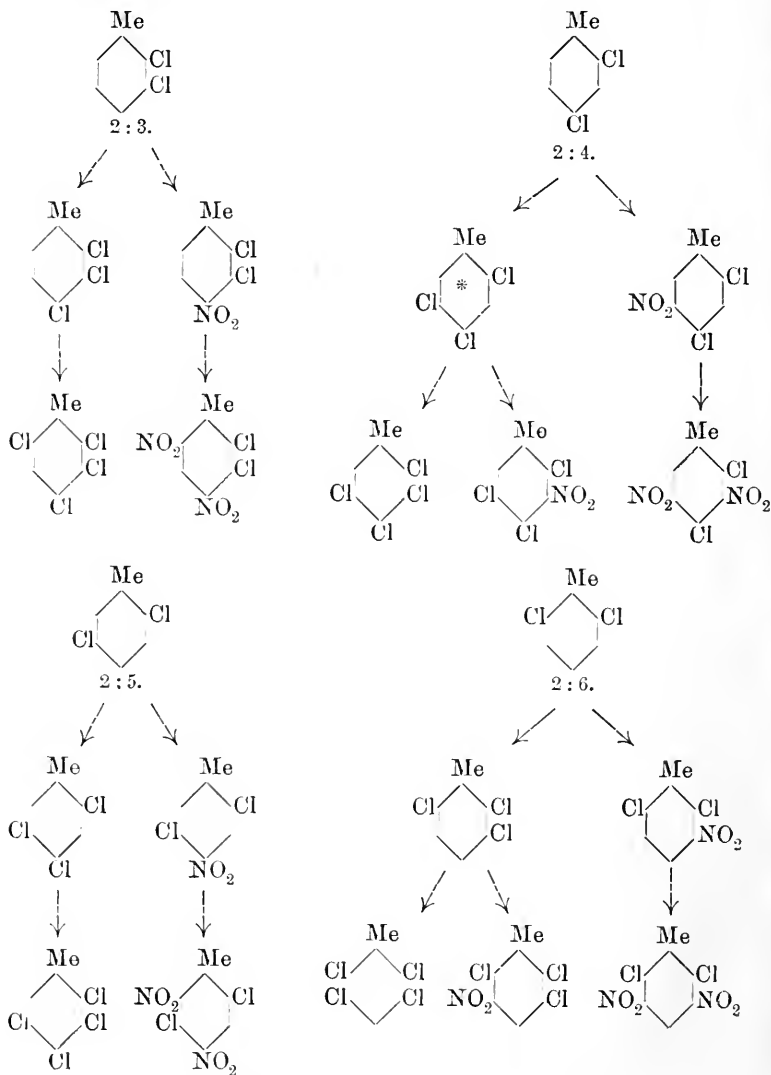
The result of the chlorination of the trichlorotoluenes is indicated by the following graphic scheme :



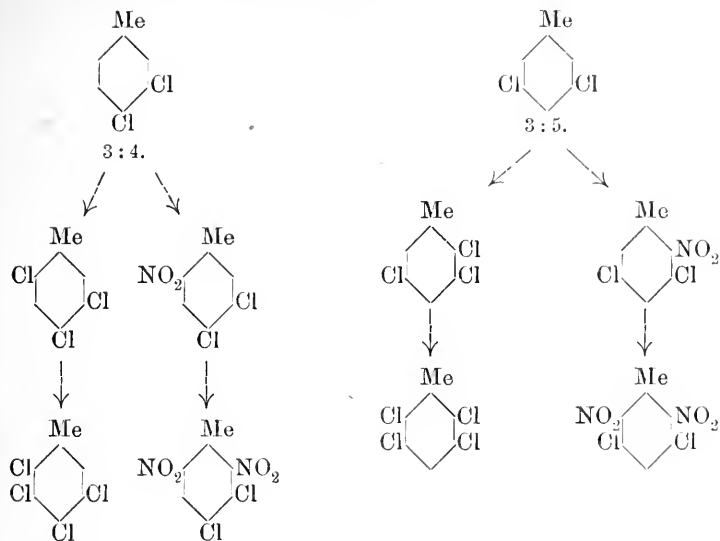
At first sight there appears to be no general law which determines the position assumed by the fourth entrant chlorine atom. It occupies both the ortho- and meta- (not, however, the para-) positions with respect to the methyl group; it enters between two contiguous chlorine atoms, between a chlorine atom and a methyl group, and again between methyl and chlorine or two chlorine atoms which are not contiguous. There is, moreover, no obvious reason why the fourth chlorine atom on entering the 3:4:5-trichloro-compound should seek a position in the side-chain. The chlorination seems to proceed in a purely arbitrary fashion.

On the other hand, there is a somewhat remarkable agreement

between the positions assumed by the third and fourth chlorine atoms on chlorination of the six dichlorotoluenes and those occupied by the first and second nitro-groups on nitration (Trans., 1902, 81, 1345); also by the fourth chlorine atom and first nitro-group effected by the chlorination and nitration of two of those trichlorotoluenes, the structure of which is known. This agreement will be apparent from the following scheme :



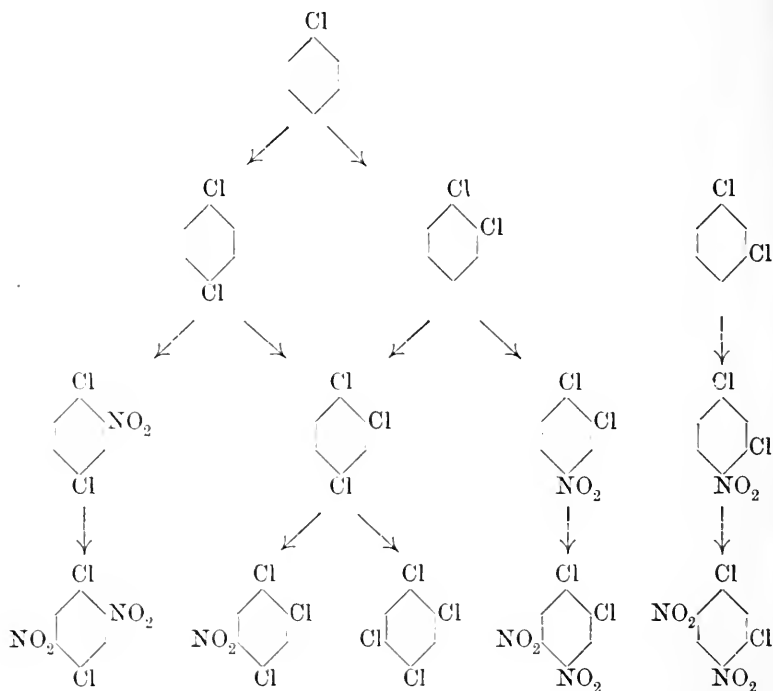
\* The main product of chlorination is taken.



There are only two exceptions to the general agreement which subsists between the products of the action of chlorine and nitric acid. In the case of the 2:5-dichlorotoluene, the 2:4:5-trichloro-compound is, according to our original observation (*Trans.*, 1902, 81, 1342), not the main product of chlorination, although it is formed at the same time; and, moreover, the fourth chlorine atom in the tetrachloro-compound should, according to the rule, occupy the ortho-position with respect to the methyl group. The other exception is the 3:4-dichlorotoluene, which gives ultimately the 2:3:4:5-tetrachloro-compound, whereas the corresponding dinitro-compound is the 3:4-dichloro-2:6-dinitrotoluene.

On closer inspection, however, it will be seen that these exceptions are correlated, for whilst the 2:4-, 2:5-, and 3:4-dichlorotoluenes give the same 2:4:5-trichlorotoluene, they each yield a different nitro-derivative. It follows, therefore, that if the second nitro-group follows the meta-law, three different dinitro-compounds must be formed, whereas the trichlorotoluene yields only one product. Agreement could only occur by the simultaneous production either of a second tetrachloro-derivative or of isomeric dinitro-compounds. Possibly a more careful examination may reveal the presence of small quantities of these products, and it will be interesting to see whether the nitro-groups in the remaining trichlorotoluenes follow the rule. Equally striking in their agreement with the above rule are the facts presented by the derivatives of dichlorobenzene, which we have taken partly from Beilstein and Kurbatoff's paper (*Annalen*, 1878, 192, 228),

and partly from our own observations. Benzene gives on chlorination *o*- and *p*-dichlorobenzenes, then, according to Jungfleisch (*Ann. Chim. Phys.*, 1869, [iv], 15, 186), Beilstein and Kurbatoff, and others, 1:2:4-trichlorobenzene and 1:2:4:5-tetrachlorobenzene, and no other isomerides. The following scheme represents the products of chlorination and nitration of the dichlorobenzenes:



The dinitro-derivatives of *ortho*- and *para*-dichlorobenzenes offer points of special interest. Hartley and Cohen (*Trans.*, 1904, 85, 869) have shown that the second nitro-group follows the meta-law completely in the case of *m*-dichlorobenzene, to the extent of about 80 per cent. in that of the *para*-compound (about 14 per cent. being *p*-dinitro *p*-dichlorobenzene), and not at all in that of the *ortho*-compound. The formation of the *p*- and *o*-dinitro-compounds is, however, in perfect harmony with the above scheme. May not the explanation of these apparent departures from the meta-law be associated in some way with the above rule?

Whatever the ultimate explanation may be, it is clear that after the first two chlorine atoms have been introduced into benzene and toluene the special rules which are usually applied to substitution are wholly or in part set aside in favour of a more general law which

includes both the chlorine atom and the nitro-group. The rule seems capable of wide and varied extension. We have already begun the repetition of Beilstein and Kurbatoff's work, which we shall extend so as to include the chlorination of *m*-dichlorobenzene. In the meantime we are tempted to predict, from the position which the nitro-group in the nitro-derivative is known to occupy, the formation of 1:2:4-trichlorobenzene and 1:2:4:5-tetrachlorobenzene from *m*-dichlorobenzene. It will, moreover, be interesting to see whether by chlorinating the isomeric chloronitrotoluenes the entrant chlorine atom occupies the same position as the first nitro-group in the nitrodichlorotoluenes, and, again, to discover whether the sulphonic groups follow the same law as the chlorine atom and nitro-groups.

### EXPERIMENTAL.

#### I. *Preparation of the Isomeric Tetrachlorotoluenes and their Derivatives.*

Before proceeding to study the action of chlorine on each of the six trichlorotoluenes, we have adopted our former plan of investigating first the properties of the pure tetrachlorotoluenes and such of their derivatives as might conveniently serve for identifying the products of chlorination.

The literature of the tetrachlorotoluenes is very scanty. By chlorinating toluene, Limpricht (*Annalen*, 1866, 139, 327) obtained a substance boiling at  $276.5^{\circ}$  and melting at  $96^{\circ}$ . Later, Beilstein and Kuhlberg (*Annalen*, 1869, 150, 286) repeated the work of Limpricht on the chlorination of toluene, which they carried out in the first stage with iodine and subsequently with antimony pentachloride as carriers. The product was fractionated, and a tetrachlorotoluene was obtained which crystallised in fine needles melting at  $91$ — $92^{\circ}$  and boiling at  $271^{\circ}$ . Further, Pieper (*Annalen*, 1867, 142, 305) prepared a liquid tetrachlorotoluene (b. p.  $280$ — $290^{\circ}$ ) by heating the additive compound,  $C_7H_6Cl_3$ , with alcoholic potash at  $110^{\circ}$ . As none of the tetrachlorotoluenes is liquid at the ordinary temperature, the substance must have been either an impure product or more probably some totally different compound.

Beilstein and Kuhlberg's compound would be either the 2:3:4:6- or 2:3:5:6-tetrachlorotoluene, which melt at  $91$ — $92^{\circ}$  and  $93$ — $94^{\circ}$  respectively, or a mixture of the two, as both substances are formed on chlorination.

The following table gives the melting points of the tetrachlorotoluenes and their nitro-compounds. We were unsuccessful in preparing other derivatives. On oxidation with nitric acid under pressure, the substances are either very slightly attacked at lower temperatures

or entirely decomposed at higher temperatures, and the corresponding tetrachlorobenzoic acids were not obtained.

Methyl = 1. Cl : Cl : Cl : Cl	Tetrachloro- toluene.	Tetrachloronitro- toluene.
2 : 3 : 4 : 5	86—88°	86—88°
2 : 3 : 4 : 6	91·5—92	131—134
2 : 3 : 5 : 6	93—94	150—152

*2 : 3 : 4 : 5-Tetrachlorotoluene.*

The tetrachlorotoluene was prepared from 2 : 4 : 5-trichlorotoluene. Eight grams of the trichlorotoluene were nitrated with 25 grams of nitric acid (sp. gr. 1·4) and 30 grams of strong sulphuric acid. The nitro-compound was separated and reduced with tin and hydrochloric acid, the base being extracted from the acid solution with chloroform. This substance diazotised very slowly. The product was poured into cuprous chloride solution and distilled in steam. The solid distillate, when crystallised from alcohol, separated in fine needles which melted at 85—87°. The melting point, after two recrystallisations, remained stationary at 86—88°.

*2 : 3 : 4 : 5-Tetrachloro-6-nitrotoluene.*—The tetrachlorotoluene was warmed with 10 parts of fuming nitric acid; the product was then poured into water and the nitro-compound crystallised from alcohol or acetic acid; it separates in flattened needles and plates which melt at 86—88°.

0·1029 gave 0·2166 AgCl. Cl = 52·1.

$C_7H_3O_2NCl_4$  requires Cl = 51·6 per cent.

*2 : 3 : 4 : 6-Tetrachlorotoluene.*

The tetrachlorotoluene was prepared from trichloroaceto-*m*-toluidide (Trans., 1902, 81, 1335) which was hydrolysed and converted into the base. Eleven grams of the base, when diazotised in the usual way and distilled in steam, yielded 11 grams of crude tetrachlorotoluene melting at 89—90°. After two crystallisations from alcohol, from which it separates in shining needles, the product melted at 91·5—92°.

0·1492 gave 0·3727 AgCl. Cl = 61·7.

$C_7H_4Cl_4$  requires Cl = 61·7 per cent.

*2 : 3 : 4 : 6-Tetrachloro-5-nitrotoluene.*—Two grams of the tetrachlorotoluene were nitrated with a mixture of 10 c.c. of nitric acid (sp. gr. 1·4) and 10 c.c. of strong sulphuric acid. The product, which crystallised from the acid solution on cooling, is sparingly soluble in alcohol, and moderately soluble in acetic acid, from which it separates in

needles melting not very sharply at  $128^{\circ}$ . After several crystallisations from alcohol, the melting point rose to  $131$ — $134^{\circ}$ . The product is still not quite pure, as may be seen from the analysis; it probably contains a little unaltered tetrachlorotoluene.

0.1107 gave 0.2355 AgCl.  $\text{Cl} = 52.6$ .

$\text{C}_7\text{H}_3\text{O}_2\text{NCl}_4$  requires  $\text{Cl} = 51.6$  per cent.

If the action of the nitric acid is prolonged so as to nitrate the product completely, a second substance is formed which appears under the microscope in the form of highly refractive rectangular plates or broad, acicular prisms according to the position of the crystal; it melts gradually at  $153^{\circ}$ . We have not investigated the compound further, but its appearance dispersed among the needles of the nitro-compound is sufficiently characteristic to have enabled us to utilise the reaction in identifying the 2 : 3 : 4 : 6-compound (p. 1284).

*2 : 3 : 5 : 6-Tetrachlorotoluene.*

The tetrachlorotoluene was prepared by nitrating 2 : 3 : 6-trichlorotoluene and replacing the nitro-group by chlorine. The trichlorotoluene was dissolved in twice its volume of fuming nitric acid (sp. gr. 1.5), which was kept cold in ice, and the product poured into water. The nitro-compound was reduced with tin and hydrochloric acid without further purification. In order to separate the base, which distils very slowly in steam, the acid solution was diluted with water and boiled, when the hydrochloride is hydrolysed and the free base, which is liquid at the boiling point of water, solidifies on cooling. The base was separated and crystallised from dilute methyl alcohol; it melts at  $66$ — $67^{\circ}$ . Six grams of trichloronitrotoluene gave 4 grams of the base. The diazotisation proceeds very slowly under ordinary conditions, and it was found necessary to use a large excess of strong hydrochloric acid and solid sodium nitrite. The quantities employed for 4 grams of the base were 15 c.c. of strong hydrochloric acid and 3 grams of finely powdered sodium nitrite. The liquid, which remains turbid from the separation of sodium chloride, was poured into the cuprous chloride solution prepared from 5 grams of copper carbonate. After the evolution of nitrogen had ceased, the tetrachlorotoluene was separated by simple filtration and well washed with water, when 3.5 grams of crude tetrachlorotoluene were obtained from 4 grams of the base. After crystallisation from methyl alcohol, it melted at  $92$ — $93^{\circ}$ , a second crystallisation raising the melting point to  $93$ — $94^{\circ}$ . The substance crystallises in opaque, white, felted needles resembling the mycelium of a fungus by the peculiar way in which the filaments cling together.

0.1524 gave 0.3801 AgCl.  $\text{Cl} = 61.6$ .

$\text{C}_7\text{H}_4\text{Cl}_4$  requires  $\text{Cl} = 61.7$  per cent.

2 : 3 : 5 : 6-*Tetrachloro-4-nitrotoluene*.—One part of the tetrachlorotoluene was dissolved in 10 parts of fuming nitric acid and heated for  $1\frac{1}{2}$  hours on the water-bath; the product was poured into water and crystallised from methyl alcohol; it forms small, hexagonal plates which melt at  $150-152^\circ$ .

0.1095 gave 0.2306 AgCl.  $\text{Cl} = 52.0$ .

$\text{C}_7\text{H}_3\text{O}_2\text{NCl}_4$  requires  $\text{Cl} = 51.6$  per cent.

## II. Chlorination of the Six Trichlorotoluenes.

The manipulative part of this section of the research offered unexpected difficulties. The preparation of the requisite quantity of each of the trichlorotoluenes has been in many cases a long and tedious operation. Moreover, the trichlorotoluenes are solids, and the use of an inert solvent in chlorinating was therefore necessary. Whilst carbon tetrachloride served this purpose excellently, provided the right proportion was used, its volatility added greatly to the difficulty of determining by the increase of weight how far the chlorination had proceeded. This is a matter of the utmost importance, as a slow reaction may yield too little of the tetrachloro-compound to identify with certainty, whereas too rapid chlorination may convert the whole of the material into higher chlorinated products. We eventually adopted the following method. A small quantity, varying from 1 to 5 grams, of the trichlorotoluene under examination was dissolved in an equal weight of carbon tetrachloride. The solution was placed in a stout test-tube provided near the top with a narrow side-piece, and connected to a second similar tube by a piece of glass-tubing which was attached to the side-tube of the first vessel and passed through the cork to the bottom of the second. Chlorine was passed for a time through the solution and the two tubes and connections then carefully counterpoised. The first tube, containing the solution, was placed in ice and the second empty tube in a good freezing mixture of ice and salt. The object of the second tube was to retain any carbon tetrachloride carried over from the first by the current of chlorine. A known weight (about 0.1 gram) of aluminium-mercury couple was then introduced into the solution, when a vigorous reaction very soon set in, which was allowed to moderate before fresh chlorine was introduced. A slow current of the dry gas was then passed through the solution until the theoretical increase in weight was obtained. The solution was left until effervescence nearly ceased and then poured off from the couple, rinsed out with fresh carbon tetrachloride into a basin, and left on the water-bath

until most of the solvent had evaporated. The residue, which solidified on cooling, was placed in a vacuum desiccator for a sufficient length of time to remove the remainder of the carbon tetrachloride. The product, which might, and usually did, contain in addition to the tetrachlorotoluene both unaltered substance and higher chlorinated compounds, was now submitted to careful fractional crystallisation from methyl alcohol, or, in some cases, to fractional sublimation on the water-bath. Less frequently it was converted directly into the nitro-derivative by heating it on the water-bath with fuming nitric acid. As a rule, a fraction melting at about 80—90° was eventually separated and in every case nitrated. The characters of the nitro-derivatives are sufficiently distinct to furnish unmistakable evidence of the constitution of the tetrachlorotoluene. It will be seen from the table on p. 1280 that there is a wide difference in the melting points of the three tetrachloronitrotoluenes, and if any doubt were likely to arise between the 2 : 3 : 4 : 6- and 2 : 3 : 5 : 6-compounds the appearance under the microscope of the two kinds of crystals in the case of the 2 : 3 : 4 : 6-compound already described would at once set the matter at rest.

*Chlorination of 2 : 3 : 4-Trichlorotoluene.*

The chlorination of 2 : 3 : 4-trichlorotoluene was conducted as already described. After fractional crystallisation from methyl alcohol, a portion melting at 89—91° was separated, which consisted of a felted mass of shining needles; a less soluble portion, consisting of hard needles and quite homogeneous in appearance, melted indefinitely at 128—165° and was not further investigated. The first fraction (m. p. 89—91°) was nitrated with fuming nitric acid on the water-bath. After crystallising the product from alcohol, it melted slowly at 153° and showed the mixture of crystals characteristic of the 2 : 3 : 4 : 6-compound. The process was repeated with a fresh quantity of trichlorotoluene, and a portion melting at 88—92° was isolated. The following experiment was then made. An equal quantity (about 0.5 gram) of the following four substances was placed in separate test-tubes, namely, the first fraction (m. p. 89—91°), the second fraction (m. p. 88—92°), 2 : 3 : 4 : 5-tetrachlorotoluene, and 2 : 3 : 4 : 6-tetrachlorotoluene. The same quantity (1 c.c.) of fuming nitric acid was added to each and the test-tubes placed in boiling-water, which was at once allowed to cool. On cooling, crystals were deposited in the tubes containing the two fractions and the 2 : 3 : 4 : 6-tetrachlorotoluene, but none in that of the 2 : 3 : 4 : 5-compound, the nitro-derivative of which is very soluble in the acid. The first three specimens were precipitated with water, crystallised once from alcohol, and the melting points determined simultaneously with the following result:—The product

from the pure 2:3:4:6-compound melted at 150°, that from the fraction (m. p. 89—91°) at 149°, and that from the fraction (m. p. 88—92°) at 145°. In all three cases, the presence of the two kinds of crystals could be detected under the microscope. In no experiment, and it was repeated four times with altogether 20 grams of material, was there any indication of a more fusible nitro-compound corresponding with the 2:3:4:5-tetrachlorotoluene.

*Chlorination of 2:3:5-Trichlorotoluene.*

The product obtained by chlorinating 2:3:5-trichlorotoluene was recrystallised and nitrated in the usual way. The following three fractions were obtained on recrystallising the nitro-compound; they melted at 148—150°, 145—147°, and 139—144°, and crystallised in hexagonal plates, characteristic of the 2:3:5:6-tetrachloronitrotoluene (m. p. 150—152°), with which the chlorination product must therefore be identified. There was no fraction melting at 86—88°, and 2:3:4:5-tetrachlorotoluene is absent.

*Chlorination of 2:3:6-Trichlorotoluene.*

After chlorination, the product was fractionally sublimed on the water-bath by heating the substance in a basin covered by a second basin containing ice-cold water; the sublimate consisted of long needles having the fungus-like appearance of the 2:3:5:6-compound. Three fractions were collected.

Fraction 1, m. p. 73—82°, gave a nitro-compound, m. p. 144—148°.

„ 2 „ 70—87° „ „ „ 148—149°.

„ 3 „ 89° „ „ „ 148—149°.

All the nitro-compounds crystallised in hexagonal plates, characteristic of 2:3:5:6-tetrachloronitrotoluene.

*Chlorination of 2:4:5-Trichlorotoluene.*

The chlorination was conducted in the usual way and the product crystallised and nitrated. The crude nitro-compound melted at 82—85°, the melting point after two crystallisations rising to 85—86°.

The melting point (86—88°) and crystalline appearance correspond with those of 2:3:4:5-tetrachlorotoluene. There was no less fusible nitro-compound, and no other tetrachlorotoluene was therefore formed.

*Chlorination of 2:4:6-Trichlorotoluene.*

If the chlorine enters the nucleus, only one derivative, namely, 2:3:4:6-tetrachlorotoluene, is possible. After chlorination, the

product was crystallised, and a fraction melting at  $89^{\circ}$  was obtained and nitrated. The nitro-compound crystallised in needles (m. p.  $125-130^{\circ}$ ) which were practically free from rectangular prisms, but, on further heating with nitric acid, the needles were almost wholly converted into rectangular prisms melting slowly at  $154^{\circ}$ , a transformation which is characteristic of the 2:3:4:6-tetrachloronitrotoluene.

*Chlorination of 3:4:5-Trichlorotoluene.*

After chlorination, the product was fractionally crystallised from methyl alcohol. Two principal fractions were obtained, a less soluble portion, which crystallised in fine silky needles and melted indefinitely from  $132^{\circ}$  to above  $150^{\circ}$ , and a second more soluble fraction, which also crystallised in needles and melted sharply at  $97-98^{\circ}$ , the melting point remaining unchanged on recrystallisation.

Fraction (m. p.  $132-150^{\circ}$ ). 0.1017 gave 0.2624 AgCl. Cl = 63.9.

$C_7H_3Cl_5$  requires Cl = 67.1 per cent.

Fraction (m. p.  $97-98^{\circ}$ ). 0.1364 gave 0.3353 AgCl. Cl = 60.9.

$C_7H_4Cl_4$  requires Cl = 61.6 per cent.

The first fraction is therefore a mixture of tetra- and penta-chlorotoluenes; the second is clearly a tetrachlorotoluene. On nitration, the latter gave a nitro-compound melting sharply at  $159^{\circ}$ . The experiment was repeated with a fresh quantity of 3:4:5-trichlorotoluene with the same result.

Now if chlorine enters the nucleus, only 2:3:4:5-tetrachlorotoluene (m. p.  $86-88^{\circ}$ ) can result, and this gives a nitro-derivative melting at the same temperature. In the present case, we have a tetrachloro-compound melting at  $97-98^{\circ}$ , which gives a nitro-compound melting at  $159^{\circ}$ . There is only one explanation possible; the fourth chlorine atom enters the side-chain. This explanation would account for the high melting point of the compound, since when chlorine enters the side-chain in toluene to form benzyl chloride, the substance is less volatile than the isomeric chlorotoluenes containing chlorine in the nucleus.

In conclusion, we wish to acknowledge our indebtedness to the Research Fund Committee of the Chemical Society for a grant which has partly defrayed the expenses of this research.

THE UNIVERSITY, LEEDS.

CXXXI.—*The Chemical Dynamics of the Reactions between Sodium Thiosulphate and Organic Halogen Compounds. Part I. Alkyl Haloids.*

By ARTHUR SLATOR, Ph.D.

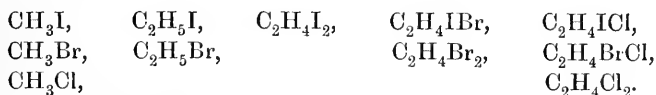
*Introduction.*

AN investigation elucidating in any way the mechanism of the reactions in which the organic haloids take part or indicating any cause for their great reactivity is of general interest owing to the extensive application of these compounds in synthetical chemistry. The reaction may be examined from the point of view of the "yield," that is, the nature and relative amounts of the different products formed under different conditions may be determined. The conclusions which can be drawn from such experiments are, however, more or less limited. Another method of investigation, which is specially applicable when the reaction takes place in a homogeneous medium, is the measurement of the reaction-velocities of the haloids with different reagents. Very definite relations exist between the velocity and the nature of a reaction, and such measurements, considered in connection with an analysis of the products of the reaction, afford probably the best means of gaining some insight into the mechanism of the reaction of these substances.

The reactivity of the alkyl haloids, especially the iodides, has been determined by such velocity measurements, and in a recent publication by Miss K. A. Burke and F. G. Donnan (*Trans.*, 1904, 85, 555), an interesting summary of this work is given. Despite the considerable number of investigations which have been carried out, the mechanism of the reactions even in these relatively simple cases is still a subject of much speculation. As pointed out by the foregoing authors, the reactivity of the haloid varies according to the reagent by which it is measured. Although qualitative resemblances may be observed between the reaction-velocities of the haloids on ethyl sodioacetoacetate (Wislicenus, *Annalen*, 1882, 212, 239), on triethylamine (Menschutkin, *Zeit. physikal. Chem.*, 1890, 5, 589), and on sodium ethoxide (Hecht, Conrad, and Brückner, *Zeit. physikal. Chem.*, 1889, 4, 273), and, again, between the velocity of decomposition of the haloids in light and the rate of their action on silver nitrate (Burke and Donnan, *loc. cit.*), yet there is a great difference between the reactivity as measured by the former set of reactions when compared with those determined by the latter. This specific nature of the velocity measurements makes it all the more difficult to

draw reliable conclusions from these experiments, and the difficulty can only be overcome by obtaining further experimental data of the reactions in which the haloids take part. I have endeavoured to bring forward more facts bearing on the problem, by measuring the reactivity of these haloids by means of another reagent. It is already known that several primary halogen compounds react with sodium thiosulphate forming the corresponding thiosulphate esters. Thus, "Bunté salt" (sodium ethyl thiosulphate) is obtained by the action of ethyl iodide according to the equation  $\text{Na}_2\text{S}_2\text{O}_3 + \text{CH}_3\text{I} = \text{NaS}_2\text{O}_3 \cdot \text{CH}_3 + \text{NaI}$ . This reaction proceeds in aqueous solution, and is probably better represented by  $\text{S}_2\text{O}_3^{2-} + \text{CH}_3\text{I} = \text{CH}_3 \cdot \text{S}_2\text{O}_3' + \text{I}^-$ . Spring and Legros (*Ber.*, 1882, 15, 1938), Purgotti (*Gazzetta*, 1892, 22, i, 416), and others, prepared the following esters by the action of a corresponding alkyl haloid on sodium thiosulphate: methyl, ethyl, propyl, *iso*-propyl, *iso*amyl, and allyl sodium thiosulphates. Ethylene chloride and glycol chlorohydrin react, forming respectively the ethylene and oxyethyl ester, and the chlorine in chloroacetic acid can also be replaced by the group  $\text{NaS}_2\text{O}_3$ . Sodium thiosulphate has no action on such compounds as ethylidene chloride, methylene chloride, and iodoform. These thiosulphate esters hydrolyse on boiling with acids giving mercaptans, showing that the alkyl group is attached to a sulphur atom in the thiosulphate molecule.

It has been found that under certain conditions the above changes proceed practically quantitatively and undisturbed by subsidiary reactions, and that, further, in many cases their velocity is measurable. Sodium thiosulphate can therefore be used as a reagent to compare the reactivities of many of the organic halogen compounds. If velocity measurements can be made with several series of compounds, some relations may be traced between reactivity and chemical constitution, and further data will also be obtained to elucidate the mechanism of these reactions. In this, the first of a series of papers on the dynamics of these reactions, the reactivities of the following compounds have been investigated by the velocity of their action on sodium thiosulphate:



The results obtained show that not only iodides but also chlorides and bromides readily act on this salt. The reactivities of the haloids lie nearer each other than is the case in the reaction with organic amines (Menschutkin, *Zeit. physikal. Chem.*, 1890, 5, 589), the ratio (iodide : bromide : chloride) in the former case being approximately 1 : 1 : 1/40, and in the latter 1 : 1/6 : 1/600.

To explain the striking reactivity of these haloids it has been suggested that they undergo some dissociation before reaction. This supposition is, however, not borne out by kinetic investigations (compare Burke and Donnan). If a haloid dissociates in water solution splitting off hydriodic acid, the acid would further dissociate, and the state of equilibrium would be greatly affected by the concentration of the  $I^-$  ion, and therefore, if such were the case, the addition of an iodide would influence the velocity of the reaction in which the haloid takes part. The results obtained in this paper show that the iodides have no appreciable influence on the reaction-velocities, and that the reactivity of the haloids toward thiosulphates in no way depends on such a dissociation.

One of the most interesting results obtained is a variation in the order of the reaction. In all cases except two, the reaction has proved to be bimolecular. With ethylene bromochloride and chloriodide, however, the velocity is dependent only on the haloid concentration, and the reaction is therefore unimolecular.

#### *General Method of Investigation.*

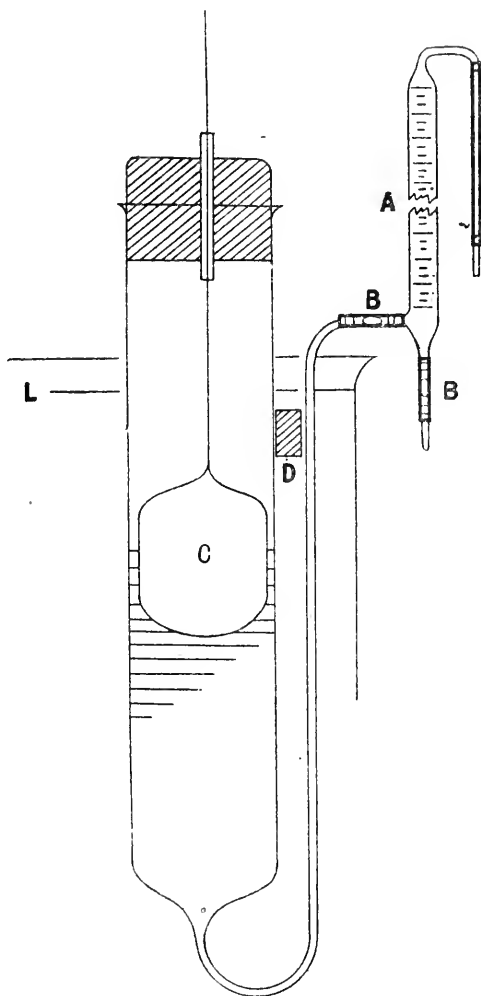
The halogen compounds used in these investigations were either obtained from Kahlbaum or prepared by standard methods.

Experiments were first carried out in order to investigate the proportions in which sodium thiosulphate and the haloids react. A weighed quantity of the latter was dissolved in alcohol and allowed to react at a suitable temperature with a known quantity of thiosulphate solution, the excess of which was titrated with standard iodine solution after the completion of the reaction. By this means, it has been shown that one equivalent of the halogen compound reacts either with one or two equivalents of sodium thiosulphate. At low temperatures, the solution remained neutral, but at higher temperatures the reaction mixture became acid, and after some time sulphur was precipitated. The acidity is due to sulphuric acid, which is formed by the hydrolysis of the thiosulphate ester. The effect of this decomposition on the iodine titration is small compared with that of the main reaction, and can in most cases be neglected.

The chief experiments described in this paper relate to velocity measurements of these reactions in dilute solution. The solvent employed in most cases was water, as nearly all the haloids are sufficiently soluble in this medium. The reaction mixture was obtained either by bringing together solutions of the two reagents, or by saturating a thiosulphate solution of suitable concentration with the haloid.

In dealing with these nearly saturated solutions of volatile halogen compounds, some difficulty was at first experienced in preventing

evaporation. This difficulty was overcome by carrying out the experiments in the vessels indicated in the diagram.



- A = small burette.
- B = Bunsen pinch-clamp.
- C = float, with wire holder.
- D = cork to support delivery tube.
- L = level of water in thermostat.

The wide glass tube contained the solution used in the experiment, and was connected with a small burette or pipette in such a manner

that 3—10 c.c. of the liquid could be quickly drawn out and titrated with iodine solution. Evaporation was hindered by protecting the surface of the solution with a float, and was entirely negligible in the lower two-thirds of the column of liquid. Where mixtures of alcohol and water were employed as solvent, this apparatus was not necessary, and the experiments were carried out in flasks.

The concentration of thiosulphate throughout the reaction was measured by titration with iodine solution, and as the products of reaction have no influence on this titration the change in concentration can be used as a measure of the rate of reaction. The iodine solution was approximately  $N/100$  ( $I/100$  grams per litre), and was standardised from time to time with sodium thiosulphate and standard dichromate solutions.

The initial concentration of sodium thiosulphate in the reacting solution varied considerably with different reactions, but was usually less than  $N/15$  ( $Na_2S_2O_3/15$  grams per litre).

The reactions were carried out with non-equivalent proportions, in most cases with an excess of thiosulphate, which was titrated at the end of the reaction. The experiments with weighed quantities showed that the concentration of the haloid could be estimated fairly correctly by means of the sodium thiosulphate titre. Measurements were carried out in a thermostat at temperatures varying from  $15^\circ$  to  $60^\circ$ , according to the velocity of reaction.

### *The Methyl and Ethyl Haloids.*

The formation of sodium methyl thiosulphate by the action of methyl iodide on sodium thiosulphate was the first of these changes to be investigated; it proceeds with a velocity very suitable for measurement, and has been examined more thoroughly than any of the reactions described later.

The reaction was found to take place nearly quantitatively, as shown by the following experiments:

0.333 gram methyl iodide required 22.8 c.c.  $N/10$  thiosulphate =  $CH_3I : 0.96 Na_2S_2O_3$ .

0.230 gram methyl iodide required 15.6 c.c.  $N/10$  thiosulphate =  $CH_3I : 0.97 Na_2S_2O_3$ .

0.0240 gram methyl iodide required 16.3 c.c.  $N/100$  thiosulphate =  $CH_3I : 0.96 Na_2S_2O_3$ .

Velocity measurements, carried out in a manner described in the previous paragraph, show that the reaction is bimolecular, the velocity being proportional to the concentrations of thiosulphate and methyl iodide.

In the following tables :

$t$  = time in minutes.

$(\text{Na}_2\text{S}_2\text{O}_3)$  = concentration of sodium thiosulphate in c.c. of the iodine solution used in the titrations (approximately  $N/100$ ).

$(\text{CH}_3\text{I})$  = corresponding concentration of the iodide.

$C_\infty$  = concentration of the excess of reacting substance (usually  $\text{Na}_2\text{S}_2\text{O}_3$ ) in gram-equivalents per litre.

$K$ , the velocity constant, is given by the usual formula for a bimolecular reaction with non-equivalent quantities,

$$K \times C_\infty = \frac{1}{t} \log c_0 c_t' / c_0' c_t,$$

where  $c_0, c_0'$  = initial concentration of the two reagents,

and  $c_t, c_t'$  = concentration after time  $t$ .

The following results were obtained with excess of thiosulphate and with excess of iodide : \*

TABLE I.—*Methyl Iodide.*

Temperature = 25°.

10 c.c. titrated. I = 0.0101N.				10 c.c. titrated. I = 0.0101N.			
Time. ( $\text{Na}_2\text{S}_2\text{O}_3$ ).	( $\text{CH}_3\text{I}$ ).	$K \times C_\infty$ .		Time. ( $\text{Na}_2\text{S}_2\text{O}_3$ ).	( $\text{CH}_3\text{I}$ ).	$K \times C_\infty$ .	
0	35.35	18.25	—	0	22.1	25.1	—
4 $\frac{3}{4}$	30.5	13.4	0.0148	5 $\frac{1}{4}$	17.6	20.6	0.0245
10	27.0	9.9	0.0148	10	14.55	17.55	0.0270
20	23.2	6.1	0.0147	20	10.6	13.6	0.0265
35	20.3	3.2	0.0147	35	7.2	10.2	0.0275
55	18.6	1.5	0.0147	55	4.9	7.9	0.0280
$\infty$	17.1	0	—	$\infty$	0	3.0	—
Mean .....			0.0147	Mean .....			0.0267
$K = \frac{0.0147 \times 10}{17.1 \times 0.0101} = 0.85.$				$K = 0.88.$			

It has been shown that in the reaction between silver nitrate and alkyl iodides an increase of the initial concentration of silver nitrate increases very considerably the velocity-constants. Such, however, is not the case in this reaction, for an increase in the concentration of the reagents brings about a slight decrease in the values of  $K$ . The following table is a summary of a number of experiments comparing the thiosulphate concentration (initial and final values are given) with the corresponding values of  $K$ :

\* The slight excess of iodide was estimated by a further addition of thiosulphate.

TABLE II.—*Methyl Iodide.*

Thiosulphate concentration at beginning and end of reaction.		Mean concentration.	$K$ .
0.048 <i>N</i>	to 0.014 <i>N</i>	0.031 <i>N</i>	0.81
0.035	„ 0.023	0.029	0.80
0.042	„ 0.014	0.028	0.78
0.035	„ 0.017	0.026	0.85
0.041	„ 0.009	0.025	0.80
0.028	„ 0.015	0.021	0.87
0.025	„ 0.007	0.016	0.87
0.025	„ 0.004	0.014	0.92
0.023	„ 0.005	0.014	0.92
0.022	„ 0.001	0.013	0.92
0.023	„ 0.000	0.013	0.87
0.022	„ 0.001	0.012	0.91
0.025	„ 0.000	0.012	0.89
0.022	„ 0.000	0.011	0.88

From this table it is evident that the change in the velocity-constant with the concentration is only very small. Further experiments were carried out where 50 c.c. of the solution were titrated, the mean concentration of the thiosulphate being about 0.003*N*. The value of  $K$  found from these experiments was almost identical with that obtained at a concentration 0.01*N*.

TABLE III.

Temperature 25°. 50 c.c. titrated.  $I = 0.0096*N*$ .

Time.	( $\text{Na}_2\text{S}_2\text{O}_3$ ).	( $\text{CH}_3\text{I}$ ).	$K \times C_\infty$ .
0	32.8	26.3	—
45	22.45	15.95	0.00119
75	18.8	12.3	0.00117
146	14.1	7.6	0.00118
270	11.0	4.5	0.00108
$\infty$	6.5	0	—
Mean .....			0.00116

$K = 0.93$  (a duplicate experiment gave 0.91). Mean = 0.92.

This slight change of the value of  $K$  with the concentration of  $\text{Na}_2\text{S}_2\text{O}_3$  can be explained if we assume that the  $\text{S}_2\text{O}_3''$  ions react according to the equation  $\text{S}_2\text{O}_3'' + \text{CH}_3\text{I} \rightarrow \text{CH}_3\cdot\text{S}_2\text{O}_3' + \text{I}'$ , whilst the undissociated  $\text{Na}_2\text{S}_2\text{O}_3$  has no direct action on methyl iodide, or reacts with a relatively much smaller velocity.

The slight increase and the final maximum in the values of  $K$ , which occur with increasing dilution, agree, at any rate, qualitatively with the change in dissociation of the sodium thiosulphate.

The assumption that the reaction is primarily connected with the  $\text{S}_2\text{O}_3''$  ion is further borne out by the effect of neutral salts on its velocity. The addition in relatively large quantities of a neutral

salt (NaCl, KCl) to a dilute sodium thiosulphate solution would increase appreciably the concentration of undissociated  $\text{Na}_2\text{S}_2\text{O}_3$ , and decrease slightly that of the  $\text{S}_2\text{O}_3^{--}$  ion. A corresponding increase or decrease should be noted in the velocity constants according as to whether the undissociated  $\text{Na}_2\text{S}_2\text{O}_3$  or the  $\text{S}_2\text{O}_3^{--}$  ion takes the main part in the reaction. The effect of such additions is a slight decrease in the values of  $K$ , as shown by the following tables:

TABLE IV.

Temperature  $25^\circ$ . 10 c.c. titrated.  $I = 0.0101N$ .

Measurements in $N/10$ KCl.				Measurements in $N/10$ $\text{NaHCO}_3$ .			
Time	$(\text{Na}_2\text{S}_2\text{O}_3)$ .	$(\text{CH}_3\text{I})$ .	$K \times C_\infty$ .	Time.	$(\text{Na}_2\text{S}_2\text{O}_3)$ .	$(\text{CH}_3\text{I})$ .	$K \times C_\infty$ .
0	25.8	23.7	—	0	26.8	18.5	—
5	21.2	19.1	0.00168	5	23.1	14.8	0.0065
10	17.7	15.6	0.00180	15	18.4	10.1	0.0067
20	13.4	11.3	0.00185	30	14.6	6.3	0.0068
60	7.25	5.15	0.00185	50	12.1	3.8	0.0068
$\infty$	2.1	0	—	$\infty$	8.3	0	—
Mean.. .....			0.00180	Mean.....			0.0067
$K = 0.85.$				$K = 0.80.$			

Measurements in  $N/10$  KI.

Time.	$(\text{Na}_2\text{S}_2\text{O}_3)$ .	$(\text{CH}_3\text{I})$ .	$K \times C_\infty$ .
0	25.3	18.8	—
5	21.8	15.3	0.0050
30	13.5	7.0	0.0052
60	10.3	3.8	0.0051
$\infty$	6.5	0	—
Mean .....			0.0051

$$K = 0.78.$$

The effect of the addition of potassium iodide is of further interest. From the above tables it is evident that large changes in concentration of the  $\text{I}'$  ion have little effect on the velocity of the reaction, and we may conclude that this  $\text{I}'$  ion plays no important part in determining the equilibria which influence this velocity (see p. 1288).

Temperature has a great effect on the velocity-constants; a rise of  $10^\circ$  trebles the velocity of the reaction. The following tables giving measurements at  $15^\circ$  and a comparison with those at  $25^\circ$  show that the temperature quotient ( $K_{t+10}/K_t$ ) is approximately 3:

TABLE V.

Temperature 15°. 10 c.c. titrated.  
I = 0.0094*N*.

Time.	(Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> ).	(CH <sub>3</sub> I).	$K \times C_{\infty}$ .
0	33.2	15.5	—
10	30.5	12.8	0.00465
25	27.45	9.75	0.00475
51	24.3	6.6	0.00460
90½	21.5	3.8	0.00465
∞	17.7	0	—

Mean..... 0.00465

$K = 0.280$ .

TABLE VI.

$K_{15}$ .	$K_{25}$ .	$K_{25}/K_{15}$ .
0.255	0.78	3.06
0.261	0.78	2.99
0.280	0.85	3.04
0.280	0.84	3.00

Mean..... 3.02

In order to give results comparable with those obtained in some later experiments, measurements were made using a mixture of alcohol and water as solvent.

The following table shows that the velocity is about 3 times as great in this solvent as in pure water:

TABLE VII.

Solvent: 25 c.c. alcohol + 10 c.c. water.

Temperature 15°. 5 c.c. titrated. I = 0.00915*N*.

Time.	(Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> ).	(CH <sub>3</sub> I).	$K \times C_{\infty}$ .
0	10.85	8.85	—
5	9.55	7.55	0.0027
15	7.7	5.7	0.0028
30	6.05	4.05	0.0028
50	4.9	2.9	0.0028
∞	2.0	0	—

Mean..... 0.0028

$K = 0.77$  (a duplicate experiment gave 0.81). Mean = 0.80.

The reactions between sodium thiosulphate and methyl bromide and chloride have also been investigated, and the following tables give a summary of the results:

TABLE VIII.—*Methyl Bromide.*

Temperature 25°.

7.5 c.c. titrated.  $I = 0.00965N$ .

Time.	(Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> ).	(CH <sub>3</sub> Br).	$K \times C_{\infty}$ .
0	20.2	10.7	—
5	17.9	8.4	0.0103
10	16.3	6.8	0.0102
20	14.0	4.5	0.0108
30	12.6	3.1	0.0111
45	11.4	1.9	0.0111
70	10.5	1.0	0.0106
$\infty$	9.5	0	—

Mean..... 0.0107

 $K = 0.88$ (Duplicate)  $K = 0.93$ 

Mean..... 0.91

Temperature 15°.

7.5 c.c. titrated.  $I = 0.0094N$ .

Time.	(Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> ).	(CH <sub>3</sub> Br).	$K \times C_{\infty}$ .
0	24.3	14.7	—
5	22.95	13.35	0.0034
15	20.5	10.9	0.0037
25	18.8	9.2	0.0036
35	17.35	7.75	0.0037
50	15.9	6.3	0.0037
71	14.35	4.75	0.0038
$\infty$	9.6	0	—

Mean..... 0.0036

 $K = 0.30$ (Duplicate)  $K = 0.285$ 

Mean..... 0.29

Temperature quotient = 3.1.

TABLE IX.—*Methyl Chloride.*

Temperature 15°.

3 c.c. titrated.  $I = 0.0103N$ .

Time.	(Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> ).	(CH <sub>3</sub> Cl).	$K \times C_{\infty}$ .
0	33.1	14.9	—
50	31.8	13.6	0.00045
170	29.45	11.25	0.00042
260	28.4	10.2	0.00037
450	25.9	7.7	0.00040
$\infty$	18.2	0	—

Mean..... 0.00041

 $K = 0.0066$ .

Temperature 25°.

2.65 c.c. titrated.  $I = 0.0118N$ .

Time.	(Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> ).	(CH <sub>3</sub> Cl).	$K \times C_{\infty}$ .
0	20.5	11.55	—
60	17.8	8.85	0.00091
105	16.6	7.65	0.00083
150	15.45	6.5	0.00085
540	11.0	2.05	0.00089
$\infty$	8.95	0	—

Mean..... 0.00087

 $K = 0.022$ .Temperature 35°. 2.65 c.c. titrated.  $I = 0.0101N$ .

Time.	(Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> ).	(CH <sub>3</sub> Cl).	$K \times C_{\infty}$ .
0	20.7	7.35	—
10	19.9	6.55	0.0033
30	18.5	5.15	0.0035
50	17.6	4.25	0.0034
187	14.55	1.2	0.0034
$\infty$	13.35	0	—

Mean..... 0.0034

 $K = 0.068$ .Temperature quotient,  $K_{25}/K_{15} = 3.3$ ,  $K_{35}/K_{25} = 3.1$ . Mean = 3.2.

The reactivity of the ethyl haloids towards sodium thiosulphate is much less than that of the methyl compounds, and although the

reaction with the iodide and bromide could be conveniently measured, the one with ethyl chloride proceeded so slowly that no exact determinations could be made. The results obtained are given in the following tables:

0.0201 gram  $C_2H_5I$  required 12.5 c.c.  $N/100$  thiosulphate =  $C_2H_5I : 0.97 Na_2S_2O_3$ .

0.0213 gram  $C_2H_5I$  required 13.5 c.c.  $N/100$  thiosulphate =  $C_2H_5I : 0.99 Na_2S_2O_3$ .

0.0610 gram  $C_2H_5Br$  required 10.75 c.c.  $N/20$  thiosulphate =  $C_2H_5Br : 0.97 Na_2S_2O_3$ .

TABLE X.—*Ethyl Iodide.*

Temperature 25°.				Temperature 35°.			
7.5 c.c. titrated. $I = 0.0096N$ .				7.5 c.c. titrated. $I = 0.0101N$ .			
Time. ( $Na_2S_2O_3$ ).	( $C_2H_5I$ ).	$K \times C_\infty$ .		Time. ( $Na_2S_2O_3$ ).	( $C_2H_5I$ ).	$K \times C_\infty$ .	
0	21.3	14.8	—	0	18.65	9.55	—
30	20.0	13.5	0.00042	30	16.3	7.2	0.00214
90	17.8	11.3	0.00043	60	14.65	5.55	0.00218
160	16.0	9.5	0.00043	95	13.4	4.3	0.00213
625	10.4	3.9	0.00041	170	11.6	2.5	0.00221
$\infty$	6.5	0	—	$\infty$	9.1	0	—
Mean.....			0.00042	Mean.....			0.00217
$K = 0.050$				$K = 0.177$			
Other expts. gave $K = 0.053, 0.048, 0.048$				Other expts. gave $K = 0.172, 0.162, 0.168$			
Mean.....			0.050	Mean.....			0.170

Temperature quotient = 3.4.

TABLE XI.—*Ethyl Bromide.*

Temperature 25°.				Temperature 50°.			
3 c.c. titrated. $I = 0.00985N$ .				7.5 c.c. titrated. $I = 0.00975N$ .			
Time. ( $Na_2S_2O_3$ ).	( $C_2H_5Br$ ).	$K \times C_\infty$ .		Time. ( $Na_2S_2O_3$ ).	( $C_2H_5Br$ ).	$K \times C_\infty$ .	
0	21.8	12.8	—	0	19.7	11.45	—
30	20.0	11.0	0.0094	6	17.9	9.65	0.0053
60	18.7	9.7	0.0090	15	15.9	7.65	0.0054
100	17.2	8.2	0.0091	35	13.05	4.8	0.0055
200	14.8	5.8	0.0088	60	11.4	3.15	0.0054
330	12.7	3.7	0.0094	91½	10.2	1.95	0.0053
545	10.9	1.9	0.0097	125	9.4	1.15	0.0054
$\infty$	9.0	0	—	$\infty$	8.25	0	—
Mean .....			0.0092	Mean .....			0.0054
$K = 0.031$ .				$K = 0.50$ .			

Temperature quotient = 3.0.

The following table is a summary of the velocity constants (at 25°) of the five reactions just described :

	I.	Br.	Cl.
CH <sub>3</sub> .....	0.90 (3.0)	0.91 (3.1)	0.022 (3.2)
C <sub>2</sub> H <sub>5</sub> .....	0.050 (3.4)	0.031 (3.0)	small

It is remarkable that the bromides and iodides react with nearly the same velocity, whilst the reactivity of the chloride is much smaller. The effect of temperature on the reaction is also of interest in that the five reactions are influenced to almost the same extent. The temperature quotient (given in brackets in the above table) varies only slightly (3.0—3.4) with the different reactions.

Some interesting comparisons might here be made between these numbers and those obtained by Menschutkin, who measured the reaction-velocities of these haloids with organic amines, but this discussion is reserved until the reactions with the higher homologues of the haloids have also been investigated.

### *The Ethylene Derivatives.*

If an ethylene haloid such as ethylene chloride is boiled with sodium thiosulphate, using as a solvent a mixture of alcohol and water, disodium ethylene thiosulphate, C<sub>2</sub>H<sub>4</sub>(NaS<sub>2</sub>O<sub>3</sub>)<sub>2</sub>, is formed. This reaction probably occurs in steps, one halogen being replaced at a time, so that a halogen ethyl ester is formed at an intermediate stage. In some cases this product seems to react immediately with another equivalent of thiosulphate and in other cases only slowly. Thus ethylene iodide and ethylene bromiodide react at 25°, using up two equivalents of thiosulphate, whilst the corresponding bromide, chlorobromide, and chloriodide, when reacting at 50°, require only one equivalent of the salt. These reactions proceed with measurable velocity, and on determining the nature of the reaction quite unexpected results were obtained. Not only do these haloids react with different equivalents of thiosulphate, but the change proceeds with some compounds (C<sub>2</sub>H<sub>4</sub>I<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>IBr, C<sub>2</sub>H<sub>4</sub>Br<sub>2</sub>) as a bimolecular reaction, whilst with others (C<sub>2</sub>H<sub>4</sub>BrCl, C<sub>2</sub>H<sub>4</sub>ICl) as a unimolecular reaction, the velocity in the latter case being independent of the thiosulphate concentration. A discussion of these results is given on p. 1303.

Ethylene iodide and ethylene bromiodide react at 25° with two equivalents of thiosulphate.

0.1325 gram C<sub>2</sub>H<sub>4</sub>I<sub>2</sub> required 18.3 c.c. N/20 thiosulphate = C<sub>2</sub>H<sub>4</sub>I<sub>2</sub>:1.94 Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.

0.0297 gram  $C_2H_4I_2$  required 20.95 c.c.  $N/100$  thiosulphate =  $C_2H_4I_2 : 1.99 Na_2S_2O_3$ .

0.0244 gram  $C_2H_4IBr$  required 20.0 c.c.  $N/100$  thiosulphate =  $C_2H_4IBr : 1.93 Na_2S_2O_3$ .

These haloids are not soluble in water, and a mixture of alcohol and water was used as a solvent. In the case of the iodide, measurements were carried out with excess of both reagents.

TABLE XII.—*Ethylene Iodide.*

Solvent: 25 c.c. alcohol + 10 c.c. water.

Temperature 25°.				Temperature 15°.			
5 c.c. titrated. I = 0.00985 <i>N</i> .				5 c.c. titrated. I = 0.00985 <i>N</i> .			
Time. ( $Na_2S_2O_3$ ).	( $C_2H_4I_2$ ).	$K \times C_\infty$ .		Time. ( $Na_2S_2O_3$ ).	( $C_2H_4I_2$ ).	$K \times C_\infty$ .	
0	14.7	11.1	—	0	13.8	18.7	—
5	12.0	5.4	0.0066	10	10.55	15.45	0.0034
15	8.9	5.3	0.0067	25	7.5	12.4	0.0034
30	6.7	3.1	0.0071	45	5.1	10.0	0.0035
55	5.2	1.6	0.0071	85	2.8	7.7	0.0036
$\infty$	3.6	0	—	$\infty$	0	4.9	—
Mean .....			0.0069	Mean .....			0.0035
			$K = 0.98$				$K = 0.36$
Duplicate expts. :				Duplicate expt. ....			
i. With excess of {				With excess of {			
thiosulphate. {				thiosulphate ... {			
ii. With excess of {				Mean ..... {			
iodide. {				0.34			
Mean .....			0.99				

From these results, it is probable that the process proceeds in steps. With ethylene iodide, the bimolecular reaction which is measured is probably  $C_2H_4I_2 + Na_2S_2O_3 = C_2H_4I \cdot NaS_2O_3 + NaI$ , followed by the reaction  $C_2H_4I \cdot NaS_2O_3 + Na_2S_2O_3 = C_2H_4(NaS_2O_3)_2 + NaI$ , which takes place rapidly as compared to the first change. Similarly, with ethylene bromide the first step is probably  $C_2H_4IBr + Na_2S_2O_3 = C_2H_4I \cdot NaS_2O_3 + NaBr$ , followed by the same reaction as with ethylene iodide. This is in accordance with the later experiments on ethylene bromide, which seem to show that the compound  $C_2H_4Br \cdot NaS_2O_3$  does not react easily with sodium thiosulphate, and the reaction is also analogous to that with alcoholic potash, where the haloid decomposes according to the equation  $C_2H_4BrI = C_2H_3I + HBr$  (Lagermark, *J. Russ. Phys. Chem. Soc.*, 1873, 5, 334).

Ethylene bromide is much less reactive than the haloids just discussed; the investigations had therefore to be carried out at higher temperatures ( $50^\circ$  and  $60^\circ$ ), when the reaction proceeded at a suitable velocity. Under these conditions the haloid was found to react with one equivalent of thiosulphate.

0.0223 gram  $C_2H_4Br_2$  required 11.9 c.c.  $N/100$  thiosulphate =  $C_2H_4Br_2 : 1.00 Na_2S_2O_3$ .

The reaction was bimolecular, as shown by the following tables:

TABLE XIV.—*Ethylene Bromide.*

Temperature $50^\circ$ .				Temperature $60^\circ$ .			
5 c.c. titrated. $I = 0.0094N$ .				5 c.c. titrated. $I = 0.00975N$ .			
Time. ( $Na_2S_2O_3$ ).	( $C_2H_4Br_2$ ).	$K \times C_\infty$ .		Time. ( $Na_2S_2O_3$ ).	( $C_2H_4Br_2$ ).	$K \times C_\infty$ .	
0	25.0	16.55	—	0	30.0	14.7	—
30	22.65	14.2	0.00079	5	28.75	13.45	0.0040
80	19.6	11.15	0.00083	10	27.5	12.2	0.0043
130	17.5	9.05	0.00082	20	25.6	10.3	0.00425
200	15.55	7.1	0.00081	40	22.85	7.55	0.00425
310	13.65	5.2	0.00075	60	20.75	5.45	0.0045
550	11.25	2.8	0.00079	90	19.05	3.75	0.0045
$\infty$	8.45	0	—	120	18.00	2.7	0.0043
Mean .....		0.00080		$\infty$	15.3	0	—
$K = 0.050$				Mean ..... $0.0043$			
From other expts. :				$K = 0.144$			
$K = 0.047, 0.051$				From other expts. :			
Mean ..... $0.049$				$K = 0.145, 0.135$			
				Mean ..... $0.141$			

Temperature quotient = 2.9.

These results indicate that the reaction, the velocity of which is measured, is  $C_2H_4Br_2 + Na_2S_2O_3 = C_2H_4Br \cdot NaS_2O_3 + NaBr$ . Attempts

made to isolate this bromoethyl ester were not successful. The very dilute solutions used in these measurements are unsuitable for preparative work, and with stronger solutions the compound seemed to undergo further change. It has been already stated that the solutions became acid during the reaction, and it seems probable that the bromoethyl ester is hydrolysed under these conditions. This view was confirmed by further experiments, in which not only the change in the concentration of thiosulphate was measured throughout the reaction, but also that in the acidity by titration with standard baryta, using phenolphthalein as an indicator.

Temp. = 50°.  $I = N/100$ .  $Ba(OH)_2 = N/100$ . 5 c.c. titrated.

Time,	( $Na_2S_2O_3$ ).	( $H_2SO_4$ ).
0 min.	19.8	0.1
15 "	18.6	0.15
45 "	16.2	0.6
100 "	13.6	1.5
185 "	11.1	2.25
320 "	8.7	3.3
24 hrs.	3.7	4.0

Inasmuch as free sulphuric acid and an odour of a mercaptan are noticeable after the reaction is completed, we may conclude that the primary reaction is followed by a hydrolysis of the thiosulphate ester.

The action of ethylene chloride on sodium thiosulphate proceeds very slowly at 50° and does not admit of accurate measurement. The reactivity according to rough measurements is about 1/90th that of the bromide.

At 50°, ethylene chlorobromide acts with measurable velocity on sodium thiosulphate and uses up one equivalent of the salt.

0.0182 gram  $C_2H_4ClBr$  required 13.0 c.c.  $N/100$  thiosulphate =  $C_2H_4ClBr : 1.02 Na_2S_2O_3$ .

0.0185 gram  $C_2H_4ClBr$  required 13.5 c.c.  $N/100$  thiosulphate =  $C_2H_4ClBr : 1.02 Na_2S_2O_3$ .

The reaction with excess of thiosulphate proceeds as a unimolecular reaction, the velocity being proportional to the concentration of the haloid and independent of that of the thiosulphate. In the following tables,  $K$ , the velocity-constant, is calculated according to the formula

$$K = \frac{1}{t} \log C_0/C_t,$$

where  $C_0$  = initial concentration of the haloid,

$C_t$  = concentration after a time  $t$ .

The values of  $K$  so obtained remain constant throughout an experiment, and are independent of the concentration of the thio-sulphate.

TABLE XV.—*Ethylene Chlorobromide.*

Temperature 50°. 5 c.c. titrated.				Temperature 50°. 3 c.c. titrated.			
Time. ( $\text{Na}_2\text{S}_2\text{O}_3$ ).	( $\text{C}_2\text{H}_4\text{ClBr}$ ).		$K$ .	Time. ( $\text{Na}_2\text{S}_2\text{O}_3$ ).	( $\text{C}_2\text{H}_4\text{ClBr}$ ).		$K$ .
0	23.1	19.8	—	0	31.0	17.9	—
30	21.2	17.9	0.00145	70	26.9	13.8	0.00160
60	19.8	16.5	0.00135	105	25.1	12.0	0.00165
120	16.6	13.3	0.00145	125	24.3	11.2	0.00165
215	12.65	9.35	0.00150	191	21.8	8.7	0.00165
390	8.4	5.1	0.00155	280	19.35	6.25	0.00165
$\infty$	3.3	0	—	367	17.85	4.75	0.00155
				500	16.10	3.0	0.00155
				$\infty$	13.1	0	—
Mean .....			0.00145	Mean .....			0.00160

Temperature 60°. 3 c.c. titrated.

Extreme values of ( $\text{Na}_2\text{S}_2\text{O}_3$ ).			$K$ .
15.8 c.c.	—	1.0 c.c.	0.0046
16.2 „	—	1.5 „	0.0046
30.0 „	—	15.3 „	0.0043
Mean .....			0.0045

Temperature quotient = 3.0.

The reaction with ethylene chloriodide is also unimolecular and proceeds with a velocity nearly thrice that obtained with the chlorobromide.

TABLE XVI.—*Ethylene Chloriodide.*

Temperature 50°. 5 c.c. titrated.				Temperature 50°. 5 c.c. titrated			
Time. ( $\text{Na}_2\text{S}_2\text{O}_3$ ).	( $\text{C}_2\text{H}_4\text{I}$ ).		$K$ .	Time. ( $\text{Na}_2\text{S}_2\text{O}_3$ ).	( $\text{C}_2\text{H}_4\text{I}$ ).		$K$ .
0	12.5	5.7	—	0	26.4	15.1	—
20	11.5	4.7	0.0042	20	25.8	12.5	0.0041
50	10.4	3.6	0.0040	40	21.6	10.3	0.0039
80	9.55	2.75	0.0040	70	19.8	8.5	0.0036
120	8.7	1.9	0.0040	100	17.85	6.55	0.0036
20 hrs.	6.8	0	—	160	15.5	4.2	0.0035
				22 hrs.	11.3	0	—
Mean .....			0.0041	Mean .....			0.0037

The end-point of this reaction was not very sharp, thus in 18—20 hours approximately one equivalent of thiosulphate was employed, whilst in 48 hours the titration corresponded with 1.3 equivalents.

From tables 15 and 16 it is evident that with excess of thiosulphate the reactions are approximately unimolecular. It is important from a theoretical point of view to know if the nature of the reaction is the

same with excess of the other reagent. The chloriodide is more reactive than the bromiodide and investigations were therefore made with it. The reactions were carried out with weighed quantities of the haloid and the end-points calculated on the basis of one equivalent of the haloid to one of thiosulphate. The order of the reaction ( $n$ ) was obtained from the initial velocities  $dc/dt$ , with concentrations of the reagents in the ratio of 2 : 1 according to the usual formula :

$$n = \frac{\log dc_1/dt - \log dc_2/dt}{\log 2}.$$

The following table shows that with a large excess of the halogen compound the order of the reaction increases to 1.85.

TABLE XVII.

Temp. 35°. Solvent : 25 c.c. alcohol + 10 c.c. water.

	Time.	(Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> ).	(C <sub>2</sub> H <sub>4</sub> ICl).	$n$ .
{	0	13.1	28.2	1.85
	35½	10.8	25.9	
{	0	6.7	14.2	
	160	3.8	11.3	

We may therefore conclude that the reaction is unimolecular with excess of thiosulphate, but approximates to a bimolecular change with excess of the halogen compound. These results may be conveniently discussed with those obtained from other ethylene compounds, a summary of which is given in the following table :

TABLE XVIII.

Haloid.	Number of Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> equivalents.	Nature of the reaction.	Velocity.	Temperature quotient for 10°.
C <sub>2</sub> H <sub>4</sub> I <sub>2</sub> .....	2	bimolecular	0.99 at 25° (a)	2.9
C <sub>2</sub> H <sub>4</sub> IBr ...	2	„	0.21 at 25° (a)	2.6
C <sub>2</sub> H <sub>4</sub> Br <sub>2</sub> ...	1	„	0.49 at 50°	2.9
C <sub>2</sub> H <sub>4</sub> ICl ...	1	*unimolecular	0.0040 at 50°	—
C <sub>2</sub> H <sub>4</sub> BrCl ..	1	„	0.00150 at 50°	3.0

\* With excess of thiosulphate.

(a) Solvent, alcohol + water.

From this summary, it is evident that the action between sodium thiosulphate and these ethylene derivatives varies considerably with the different haloids. The reactions with ethylene chloriodide and chlorobromide proceed under certain conditions as unimolecular changes, the velocity depending only on the concentration of the haloid. This

indicates that the change measured under these conditions is one involving only this compound and that the products of the change act with a relatively large velocity on the sodium thiosulphate. We can put this supposition in another form and, using an arbitrary rotation, say that " $\alpha$ "  $\text{C}_2\text{H}_4\text{ClBr}$  changes over to " $\beta$ "  $\text{C}_2\text{H}_4\text{ClBr}$  before reacting with thiosulphate, thus giving the following steps in the reaction:

1. " $\alpha$ "  $\text{C}_2\text{H}_4\text{ClBr} \longrightarrow$  " $\beta$ "  $\text{C}_2\text{H}_4\text{ClBr}$
2. " $\beta$ "  $\text{C}_2\text{H}_4\text{ClBr} + \text{Na}_2\text{S}_2\text{O}_3 \longrightarrow \text{C}_2\text{H}_4\text{Cl} \cdot \text{NaS}_2\text{O}_3 + \text{NaBr}.$

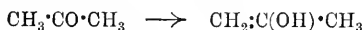
The unimolecular reaction 1 is measured in the above experiments and is followed by a rapid change 2, which uses up the " $\beta$ " compound as soon as it is formed.\* If reactions 1 and 2 proceed with comparable velocities, the order of the reaction would lie between 1 and 2. This is probably realised when the haloid is in large excess and the " $\beta$ " compound is formed too quickly to be immediately removed.

If, on the other hand, reaction 1 proceeds much more quickly than reaction 2, the equilibrium between the " $\alpha$ " and " $\beta$ " forms will be undisturbed by the latter and the change which is measured under these conditions would be the bimolecular reaction 2.

If this equilibrium between the " $\alpha$ " and " $\beta$ " compounds is such that the haloid exists for the greater part in the " $\alpha$ " form, it is clear from the law of mass action that the concentration of the " $\beta$ " form is approximately proportional to that of the total haloid. The velocity of reaction 2 would therefore be proportional to the concentration of the thiosulphate and the total haloid. It is possible that such is the case in the reactions with the first three ethylene haloids (table 18), and if this supposition is correct the mechanism of the reaction with all the five compounds is analogous, the variations in the order of the reaction depending on which step in the change proceeds the faster.

It is, however, not easy to explain reaction 1. From considerations already given, it is improbable that any of these haloids undergo dissociation, although the supposition that equation 1 represents a dissociation which takes place slowly would explain the unimolecular reaction. Another explanation which naturally suggests itself involves the assumption that the haloids can exist in two tautomeric forms, and that equation 1 represents the change of one form to the other.

\* Similar reactions have already been investigated. Thus, the hydrolysis of urea proceeds as a unimolecular reaction, a result explained by the fact that urea first changes to ammonium cyanate (C. E. Fawsitt, *Zeit. physikal. Chem.*, 1902, **41**, 601). The velocity of bromination of acetone is independent of the concentration of bromine, showing, probably, that the reaction



precedes bromination (A. Lapworth, this vol., 30).

We have, however, as yet little evidence in favour of tautomeric haloids, and such an explanation cannot be accepted without further experiments. It is remarkable that the number of equivalents of thiosulphate which take part in these reactions varies with the different ethylene haloids. This is most simply explained on the supposition of the formation of intermediate compounds having different reactivities. These are probably the halogen ethyl esters of the type  $C_2H_4X \cdot NaS_2O_3$ , the existence of which is indicated by velocity measurements. From the results given in table 18, we must conclude that the iodo-ethyl ester reacts rapidly with another equivalent of thiosulphate, whilst the corresponding bromine and chlorine compounds are not so reactive, and in dilute solution in water are hydrolysed fairly rapidly. In order to compare the reactivities of two haloids, one of which reacts with two equivalents and the other with one equivalent of the salt, the velocity coefficient of the former must be halved. Applying this correction and allowing for the influence of the solvent (table 7) and of temperature, the following numbers are obtained and are directly comparable with those given for the methyl and ethyl compounds.

$C_2H_4I_2$ .....	0.165	$C_2H_4Br_2$ .....	0.034
$C_2H_4IBr$ .....	0.035	$C_2H_4Cl_2$ .....	0.0004

The two unimolecular reactions are of course only comparable with each other.

From these tables, we see that a substitution of iodine increases the reactivity, whilst that of bromine has little effect; thus ethylene iodide is about three times more reactive than ethyl iodide, whereas ethyl and ethylene bromides react at approximately equal rates. In all probability, a substitution of chlorine decreases the reactivity, for, judging from extrapolated results, ethyl chloride is more reactive than ethylene chloride.

This investigation is being extended to reactions with other halogen compounds and salts of thiosulphuric acid, in order to obtain further reactivity-coefficients and more conclusive evidence of the mechanism of these reactions.

The author desires to express his thanks to the Research Fund Committee of the Chemical Society for a grant which defrayed some of the cost of the investigation.

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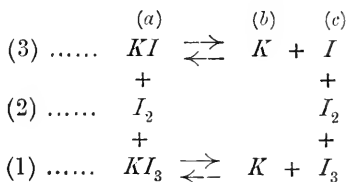
# CXXXII.—*The Nature of a Solution of Iodine in Aqueous Potassium Iodide.*

By CHARLES HUTCHENS BURGESS and DAVID LEONARD CHAPMAN.

It has been shown by Jakowkin (*Zeit. physikal. Chem.*, 1894, **13**, 539; 1896, **20**, 19) and by Dawson (*Trans.*, 1901, **79**, 238) \* that a solution of iodine in aqueous potassium iodide behaves as if it contained the compound  $KI_3$ ; and the latter authority has deduced from his own and Jakowkin's results that the ionisation constants of  $KI$  and  $KI_3$  must be equal.

The case admits, as we shall show, of two independent measurements of the migration velocities of the  $I_3$  ion being made; and since independent determinations of what ought to be, according to the theory of solutions, the same physical constant are by no means common we decided to measure and compare the two values.

To avoid ambiguity, the term ionisation is used throughout for electrolytic dissociation, and the expression dissociation is reserved for reversible chemical change which is unaccompanied by the separation of electric charges. Adopting these expressions, it can be readily shown that a simple relation subsists between the ionisation and dissociation constants of the solution under consideration. The chemical equations can be most compactly written in the following form:



The horizontal equations (1) and (3) are ionisation equations, and their equilibrium constants are denoted by  $k_1$  and  $k_3$  respectively. The columns (a) and (c) are dissociation equations, and  $k_a$  and  $k_c$  are the constants belonging to them. The quantities of the substances present are given by  $a_1, b_1, c_1, a_2, \dots, c_3$ , where the letter is the same as that of the column, and the suffix the same as that of the row in which the chemical symbol of the substance, the quantity of which it is desired to represent, occurs in the above scheme: thus  $I_3$  occurs in column (c) and row (1); the amount present in gram-molecules per litre is therefore indicated by the symbol  $c_1$ .

\* The bibliography connected with the subject is contained in this paper.

Using these symbols, the equilibrium equations become :

$$\left. \begin{array}{l} k_1 a_1 = b_1 c_1 \\ a_2 = c_2 \\ k_3 a_3 = b_3 c_3 \end{array} \right\} \text{I.} \quad \text{and} \quad \left. \begin{array}{l} k_a a_1 = a_2 a_3 \\ b_1 = b_3 \\ k_c c_1 = c_2 c_3 \end{array} \right\} \text{II.}$$

Eliminating  $c_2$  and  $b_3$  from these we obtain :

$$\left. \begin{array}{l} k_1 a_1 = b_1 c_1 \\ k_3 a_3 = b_1 c_3 \end{array} \right\} \text{and} \quad \left. \begin{array}{l} k_a a_1 = a_2 a_3 \\ k_c c_1 = a_2 c_3 \end{array} \right\} \dots \text{III.}$$

From which it immediately follows that :

$$\frac{k_1}{k_3} = \frac{c_1 a_3}{a_1 c_3} = \frac{k_a}{k_c} \quad . \quad . \quad . \quad . \quad . \quad (A)$$

The ionisation constants of  $KI_3$  and  $KI$  are therefore proportional to the dissociation constants of  $KI_3$  and  $I_3$ .

Now Jakowkin has shown that the experimental results are in agreement with an equilibrium represented by an equation of the form :

$$k(KI_3) = (KI) \times (I_2),$$

where the symbols  $(KI_3)$  and  $(KI)$  are used to denote the sum of the ionised and non-ionised gram-molecules of potassium tri-iodide and potassium iodide respectively present in unit volume of the solution. Using our symbols, the equation becomes :

$$k(a_1 + c_1) = a_2(a_3 + c_3).$$

Substituting the values of  $a_2 a_3$  and  $a_2 c_3$  from III, this reduces to :

$$k(a_1 + c_1) = k_a a_1 + k_c c_1 \quad . \quad . \quad . \quad . \quad . \quad (B),$$

and as  $a_1$  and  $c_1$  are independent and  $k$  is constant,

$$k = k_a = k_c \quad . \quad . \quad . \quad . \quad . \quad . \quad (C);$$

and from A,

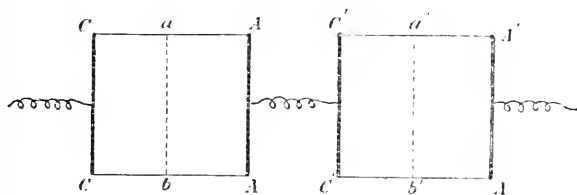
$$k_1 = k_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad (D).$$

That is, the dissociation constants of  $KI_3$  and  $I_3$  are both equal to Jakowkin's constant  $k$ , and the ionisation constants of  $KI_3$  and  $KI$  are equal to one another. It can be easily shown that the equation (D) is a necessary and sufficient condition that Jakowkin's expression,  $\frac{(KI) \times (I_2)}{(KI_3)}$ , shall have a constant value. In view of the prevailing doubt as to the applicability of the law of mass to the ionisation of strong

electrolytes, it is important to point out that no assumption has been made as to the constancy of the coefficients,  $k_1$  and  $k_3$ . All that is required of these coefficients is that they should remain sensibly equal to one another within the limits of Jakowkin's experiments.

The principle of the experimental method can now, with the aid of the foregoing relations, be described. An electric current is supposed to pass from the anode  $A'$  through a solution of iodine in potassium iodide to the cathode  $C'$ , and then from the anode  $A$  to the cathode  $C$  through a solution of potassium iodide. The planes  $ab$  and  $a'b'$  are drawn between the electrodes. After the passage of the current, iodine will have collected on the right hand side of  $ab$ , and its amount will, in accordance with Faraday's law, be a direct measure of the quantity of electricity passed. The solution between  $A'$  and  $C'$  contains free iodine at the beginning, but as the current passes the concentration of the iodine on the right hand side of  $a'b'$  increases, and, when the current is stopped this increase is found to be greater than

FIG. 1.



the amount liberated in the voltameter  $AC$ . Let  $I_2$  be the increase of free iodine on the right hand side of  $a'b'$ , and  $I_1$  the iodine liberated in the voltameter. If  $Q$  is the total quantity of electricity which passes during an experiment,  $Q = I_1$ .\* Let  $dS$  be an element of area of the plane  $a'b'$ , and  $E$  the normal electromotive intensity. The symbols  $c_3$ ,  $c_1$ , and  $b_1$  are used, as previously, to denote the number of gram-ions of iodine,  $I_3$ , and potassium respectively present in unit volume of the solution. The velocities of the  $\bar{I}$ ,  $\bar{I}_3$ , and  $K^+$  ions are respectively denoted by the symbols  $v_3$ ,  $v_1$ , and  $u$ . Let  $C$  be the current per unit area normal to the plane  $a'b'$ , the time being represented by the letter  $t$ .

Then

$$CdSdt = (c_3v_3 + c_1v_1 + b_1u)EdSdt.$$

Integrate over the whole area and between the times  $t_0$  and  $t_1$ ,

\* To avoid the introduction of a constant, the unit of electricity is taken as the charge carried by a gram-equivalent of an element.

where  $t_0$  and  $t_1$  are the times at which the experiment is started and ended, then

$$\int \int_{t_0}^{t_1} C dS dt = (c_3 v_3 + c_1 v_1 + b_1 u) \int \int_{t_0}^{t_1} E dS dt.$$

The left hand side of the equation is the total quantity of electricity which passes across the plane during the experiment, that is,  $Q$ , and, denoting the term on the right hand side under the sign of integration by  $K$ , the equation becomes:

$$I = Q = (c_3 v_3 + c_1 v_1 + b_1 u) K \quad . \quad . \quad . \quad (a).$$

Now the increase of free iodine on the right hand side of  $a'b'$  is due to the number of  $\bar{I}$  and  $\bar{I}_3$  passing from left to right of the plane, and to the number of iodine atoms set free by the movement of potassium ions from right to left. Without troubling to consider each element separately, it is readily seen that, on integrating, the total increase of iodine  $I'$  on the right hand side of  $a'b'$  is given by the equation

$$I' = (c_3 v_3 + 3c_1 v_1 + b_1 u) K \quad . \quad . \quad . \quad (b),$$

but

$$b_1 = c_1 + c_3,$$

therefore

$$I = \{c_3(v_3 + u) + c_1(v_1 + u)\} K$$

and

$$I' = \{c_3(v_3 + u) + c_1(3v_1 + u)\} K.$$

From these two equations we obtain

$$I' - I = 2Kc_1v_1$$

and

$$3I - I' = 2K\{c_3(v_3 + u) + c_1u\},$$

whence

$$\frac{I' - I}{3I - I'} = \frac{c_1v_1}{c_3(v_3 + u) + c_1u} = P \text{ say.}$$

The latter equation can be put into the form

$$P \left\{ \frac{c_3}{c_1} + \frac{u}{v_3} \left( 1 + \frac{c_3}{c_1} \right) \right\} = \frac{v_1}{v_3}.$$

Now  $P$  can be calculated from our experimental numbers,  $u/v_3$  is known from Kohlrausch's measurements, and  $c_3/c_1$  can be evaluated in the following way.

The last of the equations II (p. 1306) can be written in the form

$$\frac{c_3}{c_1} = \frac{k_c}{c_2}.$$

Where, as before,  $k_c = k = 1.00138$  and  $c_2$  is the amount of free iodine contained in the solution, which can be readily formed to any degree of approximation from Jakowkin's experimental numbers. The following table gives the calculated values of  $c_3/c_1$ ,  $P$ , and  $v_1/v_3$  for solutions containing different amounts of iodine and potassium iodide.

TABLE I.

$KI.$	$I_2.$	$c_3/c_1.$	$P.$	$v_1/v_3.$
$N/5$	$3N/50$	2.3660	0.09777	0.551
$N/10$	$3N/100$	2.3985	0.09802	0.559
$N/20$	$3N/200$	2.4628	0.09442	0.550
$N/40$	$3N/400$	2.5889	0.09124	0.554
Mean .....				0.554

We have taken 70/72 \* as the ratio of the velocities of the potassium and iodine ions.

TABLE II.

$KI.$	$I_2.$	$c_3/c_1.$	$P.$	$v_1/v_3.$
$N/5$	$3N/100$	5.7206	0.04475	0.553
$N/10$	$3N/200$	5.7746	0.04513	0.553
$N/20$	$3N/400$	5.8823	0.04509	0.567
Mean .....				0.558

*The Value of  $v_3/v_1$  obtained from Conductivity Measurements.*

Another value for the ratio of the velocities of the  $\bar{I}$  and  $\bar{I}_3$  ions can be found from a comparison of the conductivities of solutions of potassium iodide with the conductivities of solutions of potassium iodide of the same strength containing iodine. The ratio obtained in this way is not necessarily the same physical constant as that found by the method described above, for neither the ionic velocities nor the extent of the ionisation are of necessity independent of the amounts of iodine contained in the solution. We shall, however, for the present suppose that the iodine is without influence both on the ionic velocities and on the ionisation constants  $K_1$  and  $K_3$ .

$\mu_{xy}$  is used to denote the molecular conductivity† of a solution of iodine in aqueous potassium iodide which contains a gram-molecular

\* Bredig (*Zeit. physikal. Chem.*, 1894, **13**, 191) deduces the ratio 70.6/72 and Kohlrausch (*Wied. Ann.*, 1893, **50**, 385) adopts 60/63 for the same ratio at 18°.

† The solution contains both iodine and potassium iodide. The molecular conductivity here means the conductivity divided by the concentration of the potassium iodide.

weight of potassium iodide in the volume  $x$  and a gram-molecular weight of iodine in the volume  $y$ . Then, using the same symbols as before :

$$\mu_{xo} = n(u + v_3) \quad . \quad . \quad . \quad . \quad . \quad (i),$$

where  $n$  is the ratio of ionised to non-ionised molecules.

$$\mu_{xy} = n \left( u + \frac{c_3}{c_1 + c_3} v_3 + \frac{c_1}{c_1 + c_3} v_1 \right) \quad . \quad . \quad . \quad . \quad . \quad (ii).$$

$n$  has the same value in (ii) as in (i) because the ionisation constant of potassium iodide is supposed to be unaltered by the addition of iodine, whilst the ionisation constant of potassium tri-iodide has already been shown to be equal to that of potassium iodide under all conditions.

$u$  and  $v_3$  are also supposed to have the same values in (i) and (ii).

Subtracting (ii) from (i) and dividing the result by (i) we arrive at the equation :

$$\frac{\mu_{xo} - \mu_{xy}}{\mu_{xo}} = \frac{c_1}{c_1 + c_3} \cdot \frac{v_3 - v_1}{u + v_3}.$$

A simple rearrangement gives :

$$v_1/v_3 = 1 - \frac{\mu_{xo} - \mu_{xy}}{\mu_{xo}} \cdot \frac{u + v_3}{v_3} \cdot \frac{c_1 + c_3}{c_1} \quad . \quad . \quad . \quad (A).$$

Table III contains the values of  $v_1/v_3$  calculated from the measurements of M. Le Blanc and A. A. Noyes (*Zeit. physikal. Chem.*, 1890, 6, 402), and Table IV those calculated from our own measurements.

TABLE III.

$KI.$	$I_2.$	$\log. \mu_{xo} - \mu_{xy} / \mu_{xo}.$	$\log. c_1 + c_3 / c_1.$	$v_1/v_3.$
$N/2$	$N/5$	$\bar{2}.98947$	$0.4601$	$0.516$
$N/8$	$N/20$	$\bar{2}.94624$	$0.1053$	$0.556$
$N/32$	$N/80$	$\bar{2}.94134$	$0.4270$	$0.539$
$N/64$	$N/160$	$\bar{2}.84751$	$0.4542$	$0.605$
Mean .....				$0.552$

TABLE IV.

$KI.$	$I_2.$	$\log. \mu_{xo} - \mu_{xy} / \mu_{xo}.$	$\log. c_1 + c_3 / c_1.$	$v_1/v_3.$
$N/5$	$3N/100$	$\bar{2}.47881$	$0.8274$	$0.601$
$N/10$	$3N/200$	$\bar{2}.52453$	$0.8309$	$0.553$
$N/20$	$3N/400$	$\bar{2}.49644$	$0.8377$	$0.574$
$N/40$	$3N/800$	$\bar{2}.54639$	$0.8501$	$0.509$
Mean ..				$0.554$

Although the agreement amongst the individual experiments in this series is not all that might be desired, the means are perhaps suffi-

ciently close to those obtained by the other method to justify the conclusion that the two methods furnish identical values of the ratio of the velocities of the  $\bar{I}_3$  and  $\bar{I}$  ions.

#### EXPERIMENTAL.

The experimental difficulties which presented themselves were much greater than we anticipated. The particular points to which special attention had to be paid in order to obtain numbers accurate enough for our purpose are indicated below. The potassium iodide must be recrystallised if it contains traces of iodate or of alkali. The iodine was titrated with sodium thiosulphate solution of such a strength that 3 c.c., or thereabouts, corresponded with 1 c.c. of the iodine solution used in the experiment. In titrating iodine with sodium thiosulphate, care must be taken that the solution is not alkaline, as the tetrathionate at first produced by the action of the iodine on the thiosulphate is reconverted by the alkali into thiosulphate, which again reacts with the iodine, causing a considerable diminution in the quantity of thiosulphate required for the titration of a given quantity of iodine.

Although the thiosulphate usually retained its strength during an experiment, which as a rule was completed in one day, it was always titrated against a standard iodine solution during use, and a correction applied when necessary. Sodium hydrogen carbonate was never added to the thiosulphate solution in order to preserve it, as it apparently alters the titre obtained with an iodine solution of a known strength, especially when the titration is performed slowly. This effect may be due to the gradual decomposition of the hydrogen carbonate into carbonate, the presence of which has a marked influence on the titration of iodine with thiosulphate. As a rule it is not necessary in dealing with iodine solutions to take any extraordinary precautions to prevent the evaporation of iodine from solutions of this element in potassium iodide. If, however, the solutions contain a relatively small amount of potassium iodide, as in our experiments, the accuracy of the work depends more on avoiding errors from this than from any other cause. A small but appreciable amount of iodine, varying with the amount of potassium iodide present, must be contained in the solution before a colour is obtained with starch. It will be seen that the experiments were performed in such a manner that any error due to this cause was eliminated, making it unnecessary to apply a correction.

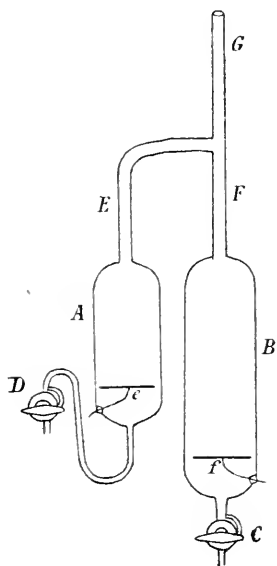
The solutions were measured with a carefully calibrated burette and two pipettes graduated against the burette which contained 50 and 25

cubic centimetres respectively. Whenever it was necessary to use a pipette, the solutions remaining in them after delivery were washed out with distilled water and added to the rest, the pipettes being calibrated for use in this way.

The voltameters were of two distinct forms according as they were intended to contain potassium iodide or a solution of iodine in potassium iodide. We shall describe these two forms as the *KI*-voltameter and the *KI<sub>3</sub>*-voltameter respectively.

Fig. II is a diagram of the *KI*-voltameter. It has two limbs, *A* and *B*, communicating with one another by two wide glass tubes, *E* and *F*. Into the bottom of each limb two platinum electrodes, *e* and *f*, are fused. To fill the voltameter, an india-rubber tube is attached to *G*, and the liquid is sucked up through the stopcocks, *C* and *D*, until its level is at a convenient distance above the junction of *E* and *F*. When the apparatus is filled with a solution of potassium iodide and a weak current passed through it with *e* as the anode and *f* as the cathode, iodine solution is formed at *e*, which, being slightly heavier than the surrounding liquid, sinks below the electrode. The iodine gradually diffuses upwards, and will in time reach the vessel *B*. Now, although an experiment need never be continued so long that this happens, it is preferable to prevent the diffusion completely by drawing through the stopcock, *D*, after the voltameter has been filled, a strong solution of potassium iodide until it covers the anode, *e*. The iodine liberated at the anode will not

FIG. II.



then diffuse beyond the boundary of the strong and weak solutions. The capillary tube leading from *A* to the tap *D* is bent in the form shown in the figure to prevent the iodine which is formed in the course of the experiment from reaching the stopcock, for then none of the iodine solution will be lost, even if the stopcock, *D*, should happen to leak slightly. We have not been able to find a lubricant for stopcocks which is entirely unacted on by iodine solutions, and have therefore dispensed with it entirely.

At the cathode, *f*, caustic potash is formed, which would, if it were not for the hydrogen which is evolved at the same time, sink to the bottom of the vessel, but, as it is, the continually escaping gas-bubbles

carry the alkali upwards, and within a few minutes from starting the experiment the alkali has found its way into the vessel *A*, the difficulty of accurately estimating the iodine being thereby considerably increased. This objectionable feature was removed by filling *B* to a short distance above the cathode with strong cadmium iodide solution. At the close of an experiment, after emptying the liquid out of *B*, the solution in *A* is run into a measured quantity of sodium thiosulphate in almost sufficient amount to remove the iodine, and the titration is then completed with thiosulphate contained in a burette. *A* is washed out first with a solution of potassium iodide and then with water, the washings being titrated with the rest. There need be no fear of the iodine volatilising if the estimation is carried out according to the directions just given. Since, as is well known, most voltameters, from a variety of causes, are liable to furnish inaccurate results, a series of experiments was performed for the purpose of testing the apparatus. Three voltameters of variable dimensions were filled with solutions of different strengths connected in series, and a current of about the same intensity as that used in the experiments passed through them. The amounts of iodine liberated in all three were always identical within the limits of the titration errors. So that it can be concluded that with a current such as we have used throughout our experiments, neither is the platinum anode attacked by the iodine nor is oxygen evolved.

The  $KI_3$ -voltameters must satisfy the following requirements: (1) It must be possible to remove from the anode limb a constant volume of solution.

(2) It must be possible to maintain a well insulated connection between them\* whilst they are in a constant temperature water-bath.

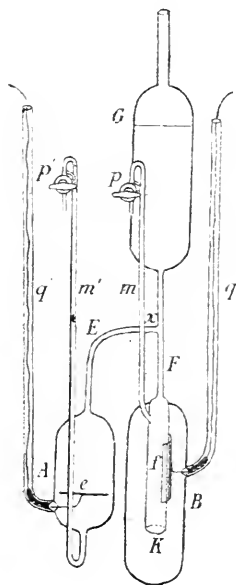
(3) Mixing of the cathodic and anodic products of electrolysis must be prevented.

The apparatus shown in Fig. III (p. 1314) was found to satisfy the above requirements admirably. It consists of two limbs, *A* and *B*, connected by capillary tubes, *E* and *F*, of about 2 mm. internal diameter. To the upper end of *F* a vessel *G* is attached, in which a supply of solution can be kept. A wide tube, *K*, open at the bottom, is fused on to the lower end of *F*, and this again is fused into *B* as shown in the diagram. The narrow bore capillary tubes *m*, *m'* serve as exit tubes from *A* and *B*, and are provided at their extremities with carefully ground capillary stopcocks, *p*, *p'*. Just above the stopcocks, the tubes are bent in the form of hooks, by which the apparatus can be conveniently suspended from the edge of the bath. The electrodes, *e*

\* For the purpose of checking the results, three voltameters connected in series were used in each experiment.

and  $f$ , of which  $e$  is the anode, are made of circular pieces of platinum foil welded to platinum wires which pass through the walls of  $A$  and  $B$ . Over the protruding ends of the platinum wires, two long glass tubes,  $q$  and  $q'$ , are fused, and bent upwards as shown in the figure. Both the inside and outside surfaces of  $q$  and  $q'$  are covered with shellac and a drop or two of mercury poured into each tube. The level of the water in the bath is adjusted so as to cover the bottom portion of the reservoir,  $G$ .

FIG. III.



Iodine solution of the required strength was made in sufficient quantity to perform three or four experiments, and was kept in vessels with well-fitting ground glass stoppers until required for use. Before beginning an experiment, the iodine contained in the solution between the joint  $x$  and the tap  $p'$  must be estimated. To do this, the tap  $p$  is closed and the solution sucked through  $p$  into  $G$ . Care must be taken that the chamber  $A$  and the capillary tubes  $E$  and  $m$  are quite free from air bubbles before closing  $p'$ . The small quantity of liquid remaining in the capillary tube below the tap is removed with a thread of cotton. The liquid in  $G$  is then allowed to run into  $B$  by opening the tap  $p$ , and after the drainage from the glass walls above  $x$  is complete, the iodine contained between  $x$  and  $p'$  is estimated in a manner similar to that adopted with the  $KI$ -voltmeter. After repeating the above estimation with two similar  $KI_3$ -volumeters, all three are suspended side by side on the edge of the water-bath.

Electrical connection is made between the anode of one voltmeter and the cathode of the next by means of an insulated wire, the ends of which are pushed down to the bottom of the tubes containing mercury, the entrance to the tubes being subsequently closed with melted paraffin wax. After passing through the three  $KI_3$ -volumeters, the current traverses a  $KI$ -voltmeter—in some of the experiments two voltmeters were used—outside the bath, and finally through an adjustable water resistance, which consisted of two small movable platinum electrodes immersed in dilute sulphuric acid.

Use was made of the town circuit of 200 volts. As a considerable variation in the current density could not in the least affect the final

results, it was considered unnecessary to include a galvanometer in the circuit. That the current density was always below the value at which oxygen or iodate would have been formed was shown by the absence of gas bubbles and by the identical titre obtained in neutral and acid solutions at the end of the experiment. It is essential that the experiment should be stopped before any change in the concentration of the solution at the junction  $x$  takes place. An estimate of the time during which it was safe to pass the current without introducing an error from this cause was obtained in the following way. The whole apparatus was set up as for an actual experiment with the electrodes of the water resistance at a fixed distance apart, the  $KI_3$ -voltameters being, however, filled with potassium iodide solution of the same concentration as the potassium iodide in the iodine solution, for which it is for the time substituted. On closing the circuit, the iodine formed at the anode can be watched and the time noted as it gradually rises in the vessel  $A$  and the capillary tube  $E$  until it almost reaches  $x$ . The time allowed for an actual experiment was at most half that required for the iodine to reach  $x$  in the above test, so that it is extremely improbable that any error was introduced by the diffusion of the products of electrolysis from the anode.

At the anode, as already stated, iodine is formed which in nearly saturated solutions crystallises out on the electrode. These crystals can easily be removed with aqueous potassium iodide at the end of the experiment, and accordingly their formation is a matter of indifference.

No hydrogen is evolved at the cathode until practically the whole of the iodine surrounding it is reduced to hydriodic acid. The reduced solution thus formed, being lighter than the original iodine solution, rises into the upper part of the space between the vessel  $B$  and the tube  $K$ , from whence it can from time to time be removed, and diffusion towards  $x$  thereby prevented by allowing this liquid to flow through the tap  $p$ .

The bath was kept at a constant temperature of  $25^\circ$  by means of a thermostat filled with a strong solution of calcium chloride, and a stirrer.

At the close of an experiment, the three  $KI_3$ -voltameters are removed from the bath and left to attain the laboratory temperature. When the cooling is complete, the iodine contained in the solution between  $x$  and the tap  $p'$  is estimated in the way already described. If any iodine should have formed on the electrode during the experiment, it ought to be removed by solution in potassium iodide as quickly as possible in order to avoid loss by volatilisation. The iodine liberated in the  $KI$ -voltameter is also estimated. The numbers so

obtained are then used as described above in the calculation of the relative velocities of the  $\bar{I}$ - and  $\bar{I}_3$ -ions. Below are the results of one experiment.

The current was passed for four hours. The solution contained  $1/20$ th of a gram-molecule of potassium iodide, and  $3/400$ th of a gram-molecule of iodine in a litre.

Titre of $KI$ -volta- meters in c.c. of $Na_2S_2O_3$ solution.	Titre of $KI_3$ -voltameters in c.c. of $Na_2S_2O_3$ solution.		
	Before experiment.	After experiment.	Difference.
I. 6.14	I. 10.73	17.38	6.65
II. 6.15	II. 10.44	17.10	6.66
	III. 10.98	17.63	6.65
Mean.....	6.145	Mean.....	6.653

In calculating the value of  $v_3/v_1$  by the formula given above, the means 6.145 and 6.653 are used, and each value of  $v_3/v_1$  in Tables I and II is the mean of three independent values so calculated.

The experimental numbers used in deducing the values contained in Tables I and II are given below:

Strength of solution in $KI_3$ -voltameters.					Strength of solution in $KI_3$ -voltameters.				
$KI$ .	$I_2$ .	$A$ .	$B$ .	$B/A$ .	$KI$ .	$I_2$ .	$A$ .	$B$ .	$B/A$ .
$N/5$	$3N/50$	8.69	10.27	1.182	$N/5$	$3N/100$	18.08	19.70	1.089
		6.30	7.39	1.173			21.52	23.37	1.086
$N/10$	$3N/100$	13.66	16.12	1.180	$N/10$	$3N/200$	10.00	10.81	1.081
		13.19	15.53	1.177			11.52	12.51	1.086
		10.90	12.84	1.178			11.31	12.28	1.085
$N/20$	$3N/200$	8.30	9.76	1.175	$N/20$	$3N/400$	13.36	14.50	1.085
		6.94	8.15	1.174			8.05	8.77	1.089
		6.84	7.98?	1.167?			6.14	6.66	1.085
$N/40$	$3N/400$	6.39	7.46	1.167			5.61	6.08	1.084
		5.69	6.64	1.167					

Under column  $A$  is the mean titre of the iodine liberated in the  $KI$ -voltameters, and under column  $B$  the mean titre of the iodine liberated in the  $KI_3$ -voltameters. The last column contains the ratio of these two quantities.

The conductivity measurements were made by Kohlrausch's method with an induction coil and telephone.

The mean value of the ratio of the velocities of the  $\bar{I}_3$ - and  $\bar{I}$ -ions determined by the voltameter method is 0.556, whereas that found by the conductivity method is 0.553.

In conclusion, it may be pointed out that the two values of the ratio of the ionic velocities have been obtained by methods which can only

be regarded as comparable if the truth of certain assumptions, and in particular of those concerning complex ions, is admitted. It was not anticipated at the outset that practically identical values would be obtained, for numerous instances of the use of the concept of complex ions to explain away difficulties in the theory of solutions, and to afford explanations of observed facts, appear to be open to doubt by reason of the difficulty of obtaining independent confirmation. It must, however, be admitted that the close agreement of two physical quantities otherwise independent is the best proof at our command of the truth of the assumptions on which their dependence rests.

THE OWENS COLLEGE,  
MANCHESTER.

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### CXXXIII.—*Note on Methyl Fluoride.*

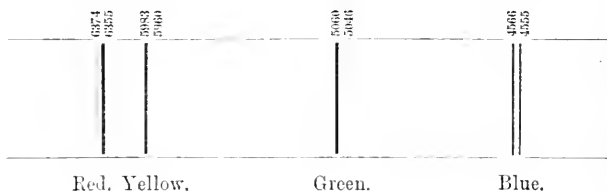
By JOHN NORMAN COLLIE.

IN a former paper (Trans., 1889, 55, 110), the author showed that by the action of heat on tetramethylammonium fluoride the salt decomposed into methyl fluoride and trimethylamine. By this reaction, nearly pure methyl fluoride was prepared. The gas was purified by freezing it to a solid by means of liquid air and removing any remaining volatile substance by means of a mercury pump. The solid was then allowed to melt slowly and boil off into a mercury gasholder, the last portion being rejected. After three of these treatments it was considered to be pure. A density determination gave 16.95 compared with hydrogen. The boiling point of the gas was determined by Prof. Travers and found to be  $-78^{\circ}$  under 742.5 mm. pressure.

Methyl fluoride is hardly attacked by strong sodium hydroxide at the ordinary temperature, three months elapsing before 20 c.c. of the gas enclosed above mercury were absorbed by a strong solution of this alkali. Sodium fluoride was found in the aqueous residue.

The chief reason for preparing the gas, however, was in order to study its spectrum. When a vacuum tube with the ordinary aluminium electrodes is filled with methyl fluoride under about 2 mm. pressure and a spark from an induction coil passed through it, a bright bluish-green colour is produced, and the spectrum, which at first consists of well-marked lines, very rapidly changes. The most important part of this spectrum is a band at 5200, a diffuse line at 5160, and two lines at 5055 and 5040. As the change takes place, the colour of the illuminated gas becomes red and the hydrogen lines appear

brilliantly. If at this point, a jar and spark gap be introduced, four pairs of lines at once appear, 6374 and 6355 in the red, 5983 and 5960 in the yellow, 5060 and 5046 in the green, and 4566 and 4555 in the blue.

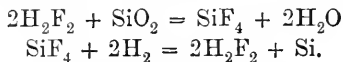


in the blue. These lines were read on a specially designed spectroscope made by Heele, and are probably correct within two or three units.

In order to study the decomposition of the gas better, it was sparked above mercury under the ordinary pressure. On the first passage of the spark, the gas was almost at once decomposed into carbon, which settled rapidly as soot on the surface of the mercury, and the volume was slightly increased. 8.1 c.c. of gas gave 10 c.c.; the product, when treated with sodium hydroxide solution, was reduced to 8.15 c.c., and the gas remaining was found to be pure hydrogen. The decomposition was evidently as follows:



The experiment was repeated and the gas sparked for about five minutes; gradually what appeared to be a filament of carbon began to grow from the negative electrode, finally bridging across the gap to the positive electrode. This filament was quite hard and tough, and would not burn away on red hot platinum foil; it was ultimately found to be pure silicon. The actual volumes in this experiment were: methyl fluoride taken, 6.4 c.c.; after sparking for about a minute, it became 8 c.c., and then gradually contracted to 4.7 c.c. Evidently the hydrofluoric acid had formed silicon fluoride with the silica of the glass; this, in its turn, was decomposed by the hydrogen present, these reactions being represented as follows:



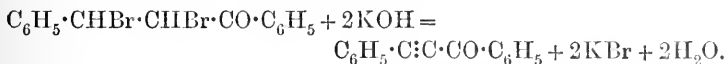
The four pairs of bright lines which were brought out by the jar and spark discharge are due to silicon fluoride. This was proved by making pure silicon fluoride and filling a comparison tube with that gas.

CXXXIV.—*Acetylenic Ketones.*

By EDWIN ROY WATSON.

NEF (*Annalen*, 1899, 308, 264) has described two acetylenic ketones, namely, benzoylphenylacetylene and acetylphenylacetylene, which he prepared by the action of benzoyl chloride and acetyl chloride respectively on sodium phenylacetylide. Moureu, who has likewise investigated these reactions (*Bull. Soc. chim.*, 1901, [iii], 25, 312), has drawn attention to the difficulty of preparing pure phenylacetylene in any quantity, and also to the fact that the simple reaction between sodium phenylacetylide and an acid chloride is always accompanied by more complicated side-reactions, which cause a decrease in the yield and purity of the acetylenic ketone produced. In following the instructions given by Nef for the preparation of benzoylphenylacetylene, I have only succeeded in obtaining a very poor yield.

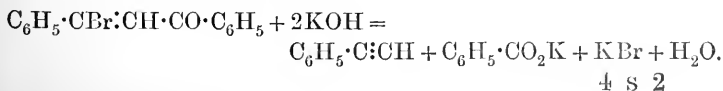
Realising the objections to this method for the production of acetylenic ketones, Dr. Ruhemann and I (this vol., p. 457) investigated the action of alcoholic potash on benzylideneacetophenone dibromide, hoping that the following reaction would occur :



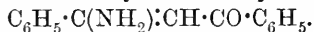
However, this change either took place and was immediately followed by the addition of a molecule of ethyl alcohol to the acetylenic ketone, or only one molecule of hydrogen bromide was removed from the dibromide with the formation of bromobenzylideneacetophenone, and then the bromine atom in this compound was directly replaced by an ethoxy-group, with the result that the substance produced was the compound  $\text{C}_6\text{H}_5\cdot\text{C}(\text{O}\cdot\text{C}_2\text{H}_5):\text{CH}\cdot\text{CO}\cdot\text{C}_6\text{H}_5$ .

At Dr. Ruhemann's suggestion, I have investigated further the chemical behaviour of bromobenzylideneacetophenone with the object of preparing from it the acetylenic ketone, benzoylphenylacetylene.

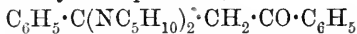
In the first place, a study of the action of caustic potash under various conditions on the bromo-compound showed that in aqueous solution this reagent had no effect, whereas the powdered solid removed a molecule of hydrogen bromide with the formation of an acetylenic linking, but at the same time the benzoyl group was eliminated, the products of the reaction being phenylacetylene, potassium benzoate, and potassium bromide :



On boiling benzylideneacetophenone dibromide with excess of pyridine for only a few minutes, one molecule of hydrogen bromide is readily removed with the formation of bromobenzylideneacetophenone. In consideration of this fact, I investigated the action of pyridine, quinoline, aniline, and other bases on bromobenzylideneacetophenone in the hope that a molecule of hydrogen bromide might also be removed from this compound, but it remained unchanged, even when heated with excess of pyridine for several hours in a closed tube at 170°. By the action of quinoline, aniline, and  $\beta$ -naphthylamine I have only been able to obtain tarry or resinous substances, whilst alcoholic ammonia gives a poor yield of aminobenzylideneacetophenone,



Piperidine readily acts on the monobromo-compound with the formation of dipiperidinobenzylacetophenone,



or  $\text{C}_6\text{H}_5 \cdot \text{CH}(\text{NC}_5\text{H}_{10}) \cdot \text{CH}(\text{NC}_5\text{H}_{10}) \cdot \text{CO} \cdot \text{C}_6\text{H}_5$ , and also piperidinobenzylideneacetophenone,  $\text{C}_6\text{H}_5 \cdot \text{C}(\text{NC}_5\text{H}_{10}) : \text{CH} \cdot \text{CO} \cdot \text{C}_6\text{H}_5$ .

It would appear that strong bases act on bromobenzylideneacetophenone so as to replace the bromine atom by an amino- or a substituted amino-group, but that with weaker bases any reaction which may occur is of a much more complicated nature.

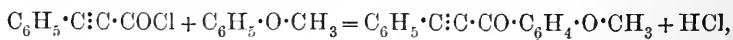
An attempt was made to split off piperidine from dipiperidinobenzylacetophenone, but distillation under reduced pressure did not yield any product of constant boiling point, and the distillate did not contain benzoylphenylacetylene.

The substance is a base and dissolves easily in hydrochloric acid forming a salt having the formula  $\text{C}_{25}\text{H}_{32}\text{ON}_2 \cdot \text{HCl}$ .

On boiling with excess of dilute hydrochloric acid, decomposition occurs with the formation of benzaldehyde, piperidine, and another substance which has not yet been further investigated (see p. 1323).

Aminobenzylideneacetophenone, when heated for some hours at 150°, did not give off ammonia forming benzoylphenylacetylene, and the product was a tarry mass.

The study of the action of bases on bromo-substituted olefinic ketones not having led to a method for the preparation of acetylenic ketones, another possible method was tried, namely, the Friedel and Crafts ketone synthesis, in this case using the chloride of an acetylenic acid. Stockhausen and Gattermann (*Ber.*, 1892, 25, 3535) had already prepared phenylpropiolyl chloride by the action of phosphorus pentachloride on phenylpropionic acid and had caused it to react with anisole in the presence of aluminium chloride, according to the equation :



an acetylenic ketone being thus produced.

In repeating the work of these investigators, I was unable to obtain any considerable quantity of pure phenylpropiolyl chloride by the action of phosphorus pentachloride on phenylpropionic acid. A considerable quantity of another acid chloride was produced, and this had a boiling point fairly near to that of phenylpropiolyl chloride, so that the yield of the latter was poor and, moreover, it was very difficult to separate the two substances. By using thionyl chloride instead of phosphorus pentachloride, according to Hans Meyer's general method (*Monatsh.*, 1901, 22, 415), it was found to be quite easy to obtain a good yield of pure phenyl propiolyl chloride.

The acid chloride reacted readily with anisole, and I was thus able to obtain the acetylenic ketone, methoxybenzoylphenylacetylene, in large quantities and in a state of purity.

The reaction occurring between phenylpropiolyl chloride and benzene in the presence of aluminium chloride is not analogous to that which takes place between the acid chloride and anisole. From the product, I isolated a hydrocarbon having the empirical formula  $C_{14}H_{12}$ , but no benzoylphenylacetylene.

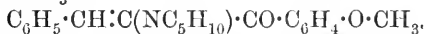
I have investigated the action of a few organic bases on the acetylenic ketones, methoxybenzoylphenylacetylene, and benzoylphenylacetylene.

With benzoylphenylacetylene, aniline gave anilinobenzylideneacetophenone,  $C_6H_5 \cdot C(NH \cdot C_6H_5) : CH \cdot CO \cdot C_6H_5$  or



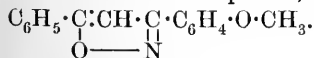
and phenylhydrazine yielded the phenylhydrazone.

With methoxybenzoylphenylacetylene, piperidine gave a compound having the empirical formula  $C_{21}H_{23}O_2N$ , which is either



The latter formula appears the more probable when we compare this substance with that obtained by the action of piperidine on bromobenzylideneacetophenone. This ketone is  $C_6H_5 \cdot CBr : CH \cdot CO \cdot C_6H_5$ , as is shown by the formation therefrom of the ethyl ether of dibenzoylmethane, and consequently the compound obtained by the action of piperidine is  $C_6H_5 \cdot C(NC_5H_{10}) : CH \cdot CO \cdot C_6H_5$ . This substance has an intensely dark red colour, whilst the compound obtained by the action of piperidine on methoxybenzoylphenylacetylene is pale yellow. It seems probable, therefore, that its constitution is not exactly analogous to that of the dark red compound.

By the action of hydroxylamine on methoxybenzoylphenylacetylene, a substance is formed which has the same percentage composition as the oxime,  $C_6H_5 \cdot C : C(NOH) \cdot C_6H_4 \cdot O \cdot CH_3$ . The substance is, however, insoluble in caustic potash, and is therefore the isooxazole derivative



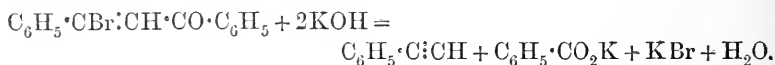
This preliminary examination of the action of bases on acetylenic ketones has been sufficient to show that additive compounds are formed by the addition of the base to the carbon atoms of the acetylenic linking. This behaviour had indeed been expected and is analogous to the addition of bases to benzylideneacetophenone, benzylideneacetylacetone, and other olefinic ketonic compounds.

### EXPERIMENTAL.

#### *The Action of Alkalis and Bases on Bromobenzylideneacetophenone.*

*The Action of Caustic Potash.*—The action of alcoholic potash, which has already been investigated (Ruhemann and Watson, *loc. cit.*), gives rise to the ethyl ether of dibenzoylmethane.

As no change occurred when the bromobenzylideneacetophenone was boiled for two hours with excess of 25 per cent. aqueous caustic potash, 3 grams of the finely powdered solid reagent, mixed in a dry flask with 5 grams of the monobromo-compound, were warmed gently on the water-bath; a vigorous reaction occurred, and the mixture set to a hard solid, which was added to excess of water and extracted with ether. The ethereal extract contained phenylacetylene together with a little of the unchanged monobromo-compound. On distillation under reduced pressure, the greater portion came over on the water-bath and gave the characteristic yellow precipitate of copper phenylacetylide on treatment with ammoniacal cuprous chloride. The aqueous solution was then acidified with dilute acid and again extracted with ether. The crystalline solid which remained on evaporating off the solvent was identified as benzoic acid. Therefore the reaction between the solid caustic potash and the bromobenzylideneacetophenone was as follows:



The same reaction occurred when solid powdered potash was left for 24 hours in contact with an ethereal solution of the bromo-substituted olefinic ketone.

*The Action of Piperidine.*—Five grams of bromobenzylideneacetophenone were dissolved in about 50 c.c. of absolute alcohol and 4–5 grams of piperidine added gradually with cooling; the mixture became red and a solid soon crystallised out. After some hours, the solid was collected, washed, and recrystallised from alcohol, being thus obtained in fine, very light yellow needles melting at 156–157°; it is *dipiperidinobenzylacetophenone*,  $\text{C}_6\text{H}_5\cdot\text{C}(\text{NC}_5\text{H}_{10})_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_5$  or  $\text{C}_6\text{H}_5\cdot\text{CH}(\text{NC}_5\text{H}_{10})\cdot\text{CH}(\text{NC}_5\text{H}_{10})\cdot\text{CO}\cdot\text{C}_6\text{H}_5$ , as shown by the following analysis:

0.2032 gave 0.5957 CO<sub>2</sub> and 0.1563 H<sub>2</sub>O. C = 79.95; H = 8.54.

0.2016 „ 13.1 c.c. moist nitrogen at 18° and 760 mm. N = 7.47.

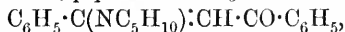
C<sub>25</sub>H<sub>32</sub>ON<sub>2</sub> requires C = 79.78; H = 8.51; N = 7.44 per cent.

This substance has basic properties and dissolves readily in cold dilute hydrochloric acid, the hydrochloride being obtained as a white precipitate by dissolving the base in dry ether and passing dry hydrogen chloride into the solution. This salt, which is very hygroscopic, was quickly collected, washed with ether, and dried in a vacuum desiccator over sulphuric acid, the percentage of hydrochloric acid being estimated by titration with decinormal silver nitrate.

0.1741 requires 4.65 c.c. N/10 AgNO<sub>3</sub>. HCl = 9.75.

C<sub>25</sub>H<sub>32</sub>ON<sub>2</sub>·HCl requires HCl = 9.74 per cent.

On evaporating under reduced pressure the alcoholic mother liquor left from the interaction of piperidine and bromobenzylideneacetophenone, a beautiful deep red substance crystallised out in heavy octahedra. This product, *piperidinobenzylideneacetophenone*,



when collected and recrystallised from absolute alcohol melted at 99–100°.

0.2031 gave 0.6161 CO<sub>2</sub> and 0.1315 H<sub>2</sub>O. C = 82.73; H = 7.19.

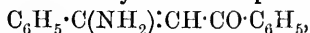
0.2055 „ 9.0 c.c. moist nitrogen at 19° and 768 mm.; N = 5.06.

C<sub>20</sub>H<sub>21</sub>ON requires C = 82.47; H = 7.21; N = 4.81 per cent.

As already stated (p. 1320), dipiperidinobenzylacetophenone did not give rise to piperidine and benzoylphenylacetylene when distilled under reduced pressure.

A solution of dipiperidinobenzylacetophenone in dilute hydrochloric acid, when boiled for some hours, yielded benzaldehyde, which was removed by extracting with ether. The acid aqueous solution, when rendered slightly alkaline, gave an oil which was taken up by ether, whilst piperidine remained in the aqueous layer.

*The Action of Ammonia.*—Ten grams of bromobenzylideneacetophenone, when dissolved in excess of strong alcoholic ammonia and left for about 24 hours, yielded cubic crystals of ammonium bromide, and then a white substance, which, after a week, was collected and washed, first with a little alcohol and then with water. On treatment with alcohol, it was found to be a mixture of two substances, one of which was sparingly soluble in alcohol, whilst the other dissolved with ease. The latter, which was in the larger proportion, was purified by repeated crystallisation from dilute alcohol, and was found to be aminobenzylideneacetophenone,



a substance previously obtained (Ruhemann and Watson, *loc. cit.*)

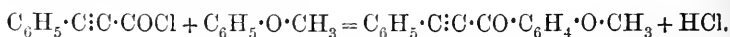
by the action of alcoholic ammonia on benzylideneacetophenone dibromide. The less soluble substance, when purified by washing with hydrochloric acid and recrystallised from boiling absolute alcohol, was obtained in fine needles melting at  $156^{\circ}$ . This compound, which contains both nitrogen and bromine, has not yet been further investigated.

*The Action of Aniline,  $\beta$ -Naphthylamine, Pyridine, and Quinoline.*

An alcoholic solution of aniline and the bromo-substituted olefinic ketone slowly yielded a tarry precipitate which could not be induced to crystallise. The behaviour of  $\beta$ -naphthylamine was very similar. Bromobenzylideneacetophenone was heated with excess of pyridine in a sealed tube at  $170^{\circ}$  for  $2\frac{1}{2}$  hours without change. On boiling a mixture of the bromo-olefinic ketone and quinoline, a vigorous reaction takes place and a tarry mass is formed.

*The Preparation of Methoxybenzoylphenylacetylene,*  
 $C_6H_5 \cdot C \equiv C \cdot CO \cdot C_6H_4 \cdot O \cdot CH_3$ .

Stockhausen and Gattermann (*Ber.*, 1892, 25, 3535) have already prepared this compound from phenylpropionic acid by transforming it into phenylpropionyl chloride and then digesting it with anisole and anhydrous aluminium chloride:



In repeating Stockhausen and Gattermann's work, I was unable, by the use of phosphorus pentachloride, to obtain a satisfactory yield of phenylpropionyl chloride. On repeatedly fractionating the products of this reaction under reduced pressure, I obtained a fraction which boiled between  $120^{\circ}$  and  $130^{\circ}$  (15 mm.) and was impure phenylpropionyl chloride, together with a larger fraction which boiled at about  $156^{\circ}$ . Twenty grams of impure acid chloride were formed from 56 grams of phenylpropionic acid, but the nature of the other product of the reaction has not yet been elucidated.

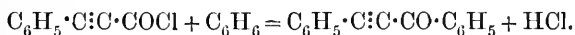
On account of the poor yield and impure state of the phenylpropionyl chloride produced by the action of phosphorus pentachloride on phenylpropionic acid, I have substituted thionyl chloride for the former substance, and, following the general directions of Hans Meyer (*Monatsh.*, 1901, 22, 415—442), I have obtained, from 40 grams of phenylpropionic acid, 25 grams of the pure acid chloride boiling at  $119^{\circ}/12$  mm.

The reaction between the acid chloride and anisole presents no difficulties and gives a good yield, namely, 22 grams of pure recryst-

tallised methoxybenzoylphenylacetylene from 25 grams of the acid chloride. The product crystallises readily from alcohol in hard prisms (m. p. 100°), dissolves in ether, carbon disulphide, or benzene, but is insoluble in light petroleum.

*The Reaction between Phenylpropiolyl Chloride and Benzene.*

It was hoped that a mixture of these substances would yield benzoyl-phenylacetylene :



Ten grams of phenylpropiolyl chloride were dissolved in excess of benzene and 20 grams of freshly prepared aluminium chloride gradually added. The evolution of hydrogen chloride which took place was not considerable; it became brisk on digesting the mixture at 50–60°, and was soon completed. The excess of benzene was then distilled off and the residue poured into a large quantity of ice-cold water, acidified with hydrochloric acid, and extracted with ether. The ethereal extract was dried and the solvent evaporated off, when the viscid residue, which was distilled under reduced pressure, was found to be a mixture of several substances; the portion which distilled between 210° and 260° (17 mm.) solidified and was purified by recrystallisation from absolute alcohol. It crystallised in broad, white prisms melting at 95°.

Analysis and a determination of the molecular weight indicated the formula  $\text{C}_{14}\text{H}_{12}$ .

0.2062 gave 0.7082  $\text{CO}_2$  and 0.1232  $\text{H}_2\text{O}$ .  $\text{C} = 93.58$ ;  $\text{H} = 6.64$ .

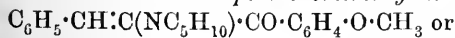
$(\text{C}_7\text{H}_6)_n$  requires  $\text{C} = 93.33$ ;  $\text{H} = 6.66$  per cent.

0.2092 in 23.88 glacial acetic acid gave  $\Delta t = -0.190^\circ$ . M. W. = 179.4.

$\text{C}_{14}\text{H}_{12}$  requires M. W. = 180.

*The Action of Organic Bases on Methoxybenzoylphenylacetylene.*

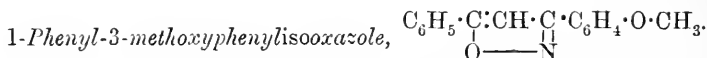
*Piperidinomethoxybenzoylstyrene,*



One molecular proportion of methoxybenzoylphenylacetylene was dissolved in sufficient alcohol in the cold and then piperidine (2 mols.) added; the mixture soon assumed a bright yellow colour, and after 36 hours, water was added, when yellow needles were precipitated. After recrystallisation from dilute alcohol, the substance was obtained in stout, light lemon-yellow needles which melted at 127°.

0.2014 gave 8.0 c.c. moist nitrogen at 22° and 754 mm.  $\text{N} = 4.44$ .

$\text{C}_{21}\text{H}_{23}\text{O}_2\text{N}$  requires  $\text{N} = 4.36$  per cent.



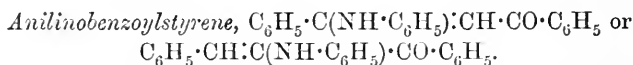
One molecular proportion of methoxybenzoylphenylacetylene was dissolved in sufficient alcohol to remain in solution on cooling, and to it was added hydroxylamine (1 mol.) in alcoholic solution. The mixture soon became brownish-yellow. After 24 hours, most of the alcohol was distilled off and the residue cooled, when a crystalline solid separated; this was collected, washed with dilute alcohol and water, and recrystallised from dilute alcohol, being thus obtained in beautiful, glistening, white plates, which melt at  $121^\circ$  and are insoluble in aqueous caustic potash.

0.2008 gave 10.0 c.c. moist nitrogen at  $22^\circ$  and 764 mm.  $N = 5.64$ .

$\text{C}_{16}\text{H}_{13}\text{O}_2\text{N}$  requires  $N = 5.57$  per cent.

*The Action of Organic Bases on Benzoylphenylacetylene.*

The benzoylphenylacetylene used for these reactions was made according to the method described by Nef (*loc. cit.*) and Moureu (*loc. cit.*).



Two grams of benzoylphenylacetylene, in the liquid form, were mixed with 1 gram of aniline. After some time, the mixture became solid, light petroleum was added, and the mixture stirred, when the whole set to a canary-coloured mass which was washed with the same liquid and recrystallised from dilute alcohol. The compound was thus obtained in thick, bright yellow prisms and melted at  $103\text{--}104^\circ$ ; it is insoluble in petroleum but dissolves readily in ether or benzene. It is insoluble in dilute hydrochloric acid even on warming.

0.1997 gave 0.6171  $\text{CO}_2$  and 0.1037  $\text{H}_2\text{O}$ .  $C = 84.27$ ;  $H = 5.76$ .

0.1968 „ 8.3 c.c. moist nitrogen at  $21^\circ$  and 758 mm.  $N = 4.78$ .

$\text{C}_{21}\text{H}_{17}\text{ON}$  requires  $C = 84.28$ ;  $H = 5.68$ ;  $N = 4.68$  per cent.

*Phenylhydrazone of Benzoylphenylacetylene,*



A mixture of the acetylenic ketone and phenylhydrazine in molecular proportions, when left for 12 hours, set to a solid which was purified by recrystallisation from methyl alcohol, being thus obtained in bright yellow leaflets melting at  $150^\circ$ .

0.2009 gave 16.4 c.c. moist nitrogen at 16° and 760 mm.  $N = 9.47$ .

$C_{21}H_{16}N_2$  requires  $N = 9.46$  per cent.

I wish to take this opportunity of expressing my thanks to Dr. Ruhemann for the valuable advice and suggestions which he has given me throughout the whole of this research.

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### CXXXV.—*A Note on Bergamot Oil and other Oils of the Citrus Series.*

By HERBERT EDWARD BURGESS and THEODORE HENRY PAGE.

#### *Bergamot Oil.*

IN continuation of our researches on oils of the *Citrus* series, we have recently examined bergamot oil, of which, up to the present time, the constituents are stated to be limonene, linalool, linalyl acetate, and limettin. To these we have been able to add acetic acid, octylene, pinene, camphene, and limene. Every care was taken to ensure that the purity of the oil used for this investigation was beyond suspicion. It had the following constants: sp. gr. 0.885 at 15°/15°;  $[a]_D + 8^\circ$ ;  $n_D$  1.4648 at 20°, these values being in accordance with the recognised figures for a pure specimen of the oil.

*Acetic Acid.*—The first fractions of bergamot oil have always a somewhat pungent odour, and on fractionation this becomes very marked in the lowest fraction. Evidently this characteristic is due to a volatile acid, for litmus paper held in the upper part of the vessel containing the fraction was markedly affected. Moreover, this fraction reacted vigorously with moist barium carbonate, and the neutral solution gave with ferric chloride a colour reaction like that of acetic acid. On analysis, the barium salt, gave the following result, which agrees closely with the number calculated for barium acetate.

0.469 barium salt gave 0.427  $BaSO_4$ .  $Ba = 53.5$ .

$Ba(CH_3 \cdot CO_2)_2$  requires  $Ba = 53.7$  per cent.

The free acid may be due to slight hydrolysis of the linalyl acetate, of which a large proportion is present in this oil, but, on the other hand, we obtained a sufficient amount from lemon oil to give qualitative tests, although this oil only contains small quantities of esters. We believe that free acetic acid is usually present in the *Citrus* oils,

for the first fractions are always somewhat pungent, although not so markedly as in the case of bergamot oil.

*Octylene*.—By careful fractionation with a 5-section modified Young's evaporator still-head, we obtained a fraction boiling between  $150^{\circ}$  and  $155^{\circ}/764$  mm., and having the following constants: sp. gr. 0.851 at  $15^{\circ}/15^{\circ}$ ,  $[\alpha]_D - 3.5^{\circ}$ ,  $n_D 1.4593$  at  $16.5^{\circ}$ .

Owing to the very small quantity, no further separation could be effected, but the constants certainly show the presence of a light substance mixed with much pinene (the next fraction). This product also had the odour of octylene, which we had previously found in lemon oil (*vide infra*).

As there was some doubt as to whether the substance found in lemon oil had not been reduced to the corresponding paraffin by distillation over sodium, this fraction was not treated with this metal, but oxidised at once with potassium permanganate solution. The light substance was completely oxidised to butyric acid, and the very small quantity of oil escaping oxidation had none of its characters, but resembled pinene; its refractive index at  $16^{\circ}$  being 1.4661. From these facts, we feel justified in calling this substance an octylene and not an octane, and we believe it to be the lowest member of the olefinic series hitherto found in essential oils.

*Pinene*.—The fraction boiling at  $157$ — $158^{\circ}/764$  mm. had sp. gr. 0.859 at  $15^{\circ}/15^{\circ}$ ,  $[\alpha]_D - 8.3^{\circ}$ ,  $n_D 1.4660$  at  $16.5^{\circ}$ .

By treatment with dry hydrogen chloride, the characteristic hydrochloride (m. p.  $125^{\circ}$ ) was obtained.

*Camphene*.—The fraction boiling at  $164$ — $165^{\circ}/764$  mm. had sp. gr. 0.868 at  $15^{\circ}/15^{\circ}$ ,  $[\alpha]_D - 22.8^{\circ}$ ,  $n_D 1.4766$  at  $16.5^{\circ}$ .

By treatment with glacial acetic acid and a small quantity of sulphuric acid in the usual way, we obtained from this fraction isoborneol (m. p.  $203^{\circ}$ ), but the quantity was too small to allow of further purification, and it is only by crystallising large quantities that the correct melting point,  $212^{\circ}$ , can be reached.

*Limonene*.—This terpene, one of the well-known constituents of bergamot oil, we obtained with a rotation of  $+88^{\circ}30'$  in a 100 mm. tube.

*Limene*.—After the removal of the linalyl acetate, we obtained a small fraction which gave the characteristic hydrochloride (m. p.  $79^{\circ}$ ) on treatment with dry hydrogen chloride in dry ether (this vol., p. 414).

### *Lemon Oil.*

*Octylene*.—In examining the most volatile terpenes from very large quantities of lemon oil, we obtained by repeated fractionation a substance having the following properties: b. p.  $123$ — $124^{\circ}/768$  mm.;

sp. gr. 0.7275 ;  $[\alpha]_D \pm 0$  ;  $n_D$  1.4066 at  $15^\circ$  ; mol. refraction, 38.54 ; the value calculated for  $C_8H_{18}$  being 38.87, and for  $C_8H_{16}$ , 38.28.

0.2580 gave 0.7936  $CO_2$  and 0.3594  $H_2O$ . C = 83.89 ; H = 15.48.

$C_8H_{18}$  requires C = 84.21 ; H = 15.79 per cent.

Vapour density determinations by Victor Meyer's method gave the numbers 112 and 117 for the molecular weight. A bromination showed that only about one-fifth of a mol. of bromine was taken up by 1 mol. of the substance : 0.406 gram of the compound absorbed 0.12 gram of bromine. All these facts seem to point to the substance being one of the octanes. On the other hand, another portion treated with potassium permanganate gave butyric acid, recognised by its odour and by the analysis of the silver salt.

0.1025 gave 0.0565 Ag. Ag = 55.12.

$C_3H_7 \cdot CO_2Ag$  contains Ag = 55.38 per cent.

This contradictory result is explained by the fact that the latter portion had not been distilled over sodium. The other portion had been thus treated to remove oxygenated impurities before its nature was suspected, and had become reduced from an octylene to an octane. This explanation is supported by the behaviour of the corresponding fraction of bergamot oil, as already mentioned.

We have evidence which makes it probable that octylene is a normal constituent of the *Citrus* oils.

#### *Distilled Oil of Limes.*

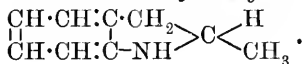
In continuation of our work on this oil (this vol., p. 414), we have been able to separate the phenylurethane of a second substance having a somewhat lower boiling point than ordinary terpineol from that fraction, which has the distinctive odour of this oil in a marked degree. The phenylurethane is more soluble than that of ordinary terpineol, and was found in the residue left after distilling off in steam the excess of terpineol from the filtrate obtained in the preparation of the urethane. It crystallised in tufts of needles, melted at  $132^\circ$ , and gave on hydrolysis a small quantity of oil having the peculiar odour of distilled oil of limes.

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dihydro- $\alpha$ -methylindole, a base somewhat related to *ac*-tetrahydro- $\beta$ -naphthylamine, in the hope of obtaining further evidence bearing on the occurrence of such tautomerism.

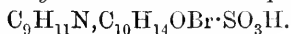
*Preparation and Resolution of Dihydro- $\alpha$ -methylindole,*



$\alpha$ -Methylindole (50 grams) is completely reduced to its dihydro-derivative when heated for 24 hours on the water-bath with tin (100 grams) and concentrated hydrochloric acid (200 grams); after rendering alkaline with caustic soda and distillation in a current of steam, extraction with ether and fractional distillation, the base is obtained as a colourless oil boiling at 225—226°.

On evaporating an aqueous solution of *d*-bromocamphorsulphonic acid with the requisite quantity of the reduced base, a certain amount of decomposition occurs, and the syrupy residue can only be caused to crystallise with difficulty. It is advisable in this case, and also in those of other bases which are not very stable, to evaporate the concentrated solution of *d*-bromocamphorsulphonic acid prepared by Pope and Peachey's method (*Trans.*, 1899, 75, 895) several times on the water-bath with the addition of alcohol, in order to drive off as much of the water as possible; under these conditions, the free acid frequently crystallises out. To the concentrated alcoholic solution of the acid thus obtained, the calculated quantity of dihydro- $\alpha$ -methylindole is added, the solution evaporated to a syrupy consistency, and the residue allowed to remain during several days in the desiccator. The mass slowly solidifies to a viscid, crystalline paste, and is then systematically crystallised fractionally from boiling ethyl acetate; it is thus resolved into a sparingly soluble salt melting at 179·5—180·5° and a readily soluble salt melting at 124—125°; the former salt is obtained pure in rather larger quantity than the latter, but, owing to the difficulty of purifying the more soluble salt, we have been unable to ascertain the relative proportion in which the two salts are actually produced. The sparingly soluble salt yields lævorotatory dihydro- $\alpha$ -methylindole when treated with alkali, and is therefore *l*-dihydro- $\alpha$ -methylindole *d*-bromocamphorsulphonate.

*l*-Dihydro- $\alpha$ -methylindole *d*-Bromocamphorsulphonate,



This salt is obtained in a pure state after about eight crystallisations of the crude crystalline deposit from boiling ethyl acetate; it is only moderately soluble in the latter medium, and crystallises therefrom in

long, colourless needles melting at  $179.5-180.5^{\circ}$ . It undergoes no loss in weight at  $100^{\circ}$  and gave the following analytical results:

0.2916 gave 0.1614  $H_2O$  and 0.5508  $CO_2$ .  $H = 6.15$ ;  $C = 51.50$ .

$C_{19}H_{26}O_4NBrS$  requires  $H = 5.85$ ;  $C = 51.35$  per cent.

The following determinations of rotatory power were made with different preparations:

0.5354 gram, made up to 25 c.c. with water, gave  $\alpha_D + 2.685^{\circ}$  in a 2 dm. tube; whence  $[\alpha]_D + 62.68^{\circ}$  and  $[M]_D + 278.3^{\circ}$ .

0.4761 gram, made up to 25 c.c. with water, gave  $\alpha_D + 2.38^{\circ}$  in a 2 dm. tube; whence  $[\alpha]_D + 62.5^{\circ}$  and  $[M]_D + 277.4^{\circ}$ . The mean value of  $[M]_D$  is thus  $+278^{\circ}$ .

In order that some idea might be obtained as to what proportion of the mean molecular rotatory power,  $[M]_D + 278^{\circ}$ , is attributable to the basic ion, 0.71 gram of the salt was boiled with a very slight excess of the theoretical quantity of caustic soda solution until all the base had volatilised, and the rotatory power of the residual solution was measured in a 2 dm. tube after making up to 50 c.c. with water, when the value  $\alpha_D + 1.74^{\circ}$  was obtained. This corresponds with  $[\alpha]_D + 61.3^{\circ}$  and  $[M]_D + 272^{\circ}$  calculated on the molecular weight of the salt. It is thus indicated that the *l*-dihydro- $\alpha$ -methylindoleammonium ion has a low molecular rotatory power of the order of  $[M]_D + 5^{\circ}$ .

*l*-Dihydro- $\alpha$ -methylindole,  $C_9H_{11}N$ .

On adding a slight excess of caustic soda to the aqueous solution of the foregoing salt, extracting with ether, and distilling in the usual way after washing and drying, *l*-dihydro- $\alpha$ -methylindole is obtained as a colourless oil, which shows a slight blue fluorescence and boils at  $228-229^{\circ}$ . The rotatory power was found to increase gradually during several hours after distillation, but, after the lapse of 4 hours, had attained a constant value, namely,  $\alpha_D - 13.61^{\circ}$  in a 1 dm. tube at  $21^{\circ}$ ; it may be noted that a progressive change in rotatory power, extending over several hours after distillation, is not uncommonly met with amongst saturated closed chain nitrogen bases, and is probably attributable to the circumstance that the material, which is unassociated in the vaporous state, only slowly becomes associated after condensation to the liquid form. It is a remarkable fact that whilst the base is levorotatory, both when free from solvent and in dry ethereal solution, it is dextrorotatory in both ethyl alcoholic and benzene solutions, as is shown by the following numbers:

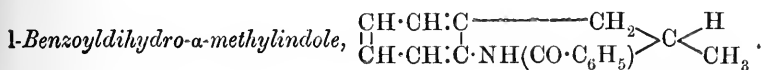
0.9512 gram, made up to 25 c.c. with absolute ethyl alcohol, gave  $\alpha_D + 0.55^{\circ}$  in a 2 dm. tube; whence  $[\alpha]_D + 7.22^{\circ}$  and  $[M]_D + 9.60^{\circ}$ .

1.0495 gram, made up to 20 c.c. with dry ether, gave  $\alpha_D - 1.42^\circ$  in a 2 dm. tube; whence  $[\alpha]_D - 13.53^\circ$  and  $[M]_D - 18.0^\circ$ .

0.6937 gram, made up to 20 c.c. with benzene, gave  $\alpha_D + 0.57^\circ$  in a 2 dm. tube; whence  $[\alpha]_D + 8.25^\circ$  and  $[M]_D + 11.0^\circ$ .

0.8336 gram, made up to 20 c.c. with benzene, gave  $\alpha_D + 0.65^\circ$  in a 2 dm. tube; whence  $[\alpha]_D + 7.8^\circ$  and  $[M]_D + 10.4^\circ$ . The mean values in benzene solution are thus  $[\alpha]_D + 8.02^\circ$  and  $[M]_D + 10.7^\circ$ .

In order to ascertain that no optical inversion attends the distillation of the base, 4.44 grams of *l*-dihydro- $\alpha$ -methylindole *d*-bromocamphorsulphonate were treated with a slight excess of aqueous caustic soda and the solution extracted several times with benzene, the benzene extracts being subsequently mixed and made up to 25 c.c. This solution gave  $\alpha_D + 0.83^\circ$  in a 2 dm. tube; whence the constants  $[\alpha]_D + 7.80^\circ$  and  $[M]_D + 10.4^\circ$  are calculated for the base contained in the salt used. The identity of these values with those obtained with benzene solutions of the distilled base proves that no optical inversion attends the distillation.



The benzoyl derivative of the active base is readily obtained by applying the Schotten-Baumann reaction to either the free base or its *d*-bromocamphorsulphonate. It crystallises from alcohol in colourless needles melting at  $119^\circ$ ; the corresponding externally compensated compound was prepared by Bamberger and Sternitzki (*Ber.*, 1893, 26, 1303) and melts at  $91.5^\circ$ .

0.1286 gave 0.0790  $\text{H}_2\text{O}$  and 0.3800  $\text{CO}_2$ .  $\text{C} = 80.51$ .  $\text{H} = 6.82$ .

$\text{C}_{16}\text{H}_{15}\text{ON}$  requires  $\text{C} = 81.01$ ;  $\text{H} = 6.33$  per cent.

0.4111 gram, made up to 25 c.c. with absolute ethyl alcohol, gave  $\alpha_D - 1.22^\circ$  in a 2 dm. tube; whence  $[\alpha]_D - 37.1^\circ$  and  $[M]_D - 87.9^\circ$ .

0.2945 gram, made up to 20 c.c. with absolute ethyl alcohol, gave  $\alpha_D - 1.09^\circ$  in a 2 dm. tube; whence  $[\alpha]_D - 37.0^\circ$  and  $[M]_D - 87.6^\circ$ .

The mean values for the substance in alcoholic solution are therefore  $[\alpha]_D - 37.05^\circ$  and  $[M]_D - 87.75^\circ$ .



On dropping acetyl chloride on to *l*-dihydromethylindole, allowing the product to remain in a vacuum desiccator, extracting with light petroleum, and evaporating the petroleum solution, *l*-acetyldihydro- $\alpha$ -methylindole is obtained, whilst a residue of the hydrochloride of the parent base remains as a crystalline powder insoluble in the solvent.

The acetyl derivative crystallises from petroleum in lustrous needles melting at  $89^{\circ}$ ; it closely resembles the externally compensated isomeride which was prepared by Jackson (*Ber.*, 1881, 14, 883), and melts at  $55-56^{\circ}$ .

0.2080 gave 0.1427  $\text{H}_2\text{O}$  and 0.5762  $\text{CO}_2$ .  $\text{C} = 75.54$ .  $\text{H} = 7.62$ .

$\text{C}_{11}\text{H}_{13}\text{ON}$  requires  $\text{C} = 75.42$ ;  $\text{H} = 7.42$  per cent.

0.2713 gram, made up to 20 c.c. with absolute ethyl alcohol, gave  $\alpha_D - 1.68^{\circ}$  in a 2 dm. tube; whence  $[\alpha]_D - 61.9^{\circ}$  and  $[\text{M}]_D - 108.4^{\circ}$ .

### *l-Dihydro- $\alpha$ -methylindole Hydrochloride*, $\text{C}_9\text{H}_{11}\text{N}, \text{HCl}$ .

On treating *l*-dihydro- $\alpha$ -methylindole with strong hydrochloric acid and allowing the mixture to remain in a vacuum desiccator, the hydrochloride separates, and, after crystallisation from benzene, is obtained in colourless, transparent needles melting at  $58^{\circ}$ . It is very soluble in water and crystallises with difficulty from this solvent; the crystals, when dried at  $100^{\circ}$ , lose about 6 per cent. in weight, corresponding with nearly half a molecule of water.

0.5130 dried salt gave 0.1093  $\text{Cl}$  on titration.  $\text{Cl} \approx 21.3$ .

$\text{C}_9\text{H}_{12}\text{NCl}$  requires  $\text{Cl} \approx 20.9$  per cent.

0.8304 gram, made up to 20 c.c. with water, gave  $\alpha_D + 0.14^{\circ}$  in a 2 dm. tube; whence  $[\alpha]_D + 1.68^{\circ}$  and  $[\text{M}]_D + 2.83^{\circ}$ .

0.6728 gram, made up to 20 c.c. with water, gave  $\alpha_D + 0.10^{\circ}$  in a 2 dm. tube; whence  $[\alpha]_D + 1.48^{\circ}$  and  $[\text{M}]_D + 2.50^{\circ}$ . The mean molecular rotatory power of the salt is thus  $[\text{M}]_D + 2.65^{\circ}$ ; this small value accounts for the fact that the molecular rotatory power of *l*-dihydro- $\alpha$ -methylindole *d*-bromocamphorsulphonate differs but little from that of the acid ion in aqueous solution.

### *Derivatives of d-Dihydro- $\alpha$ -methylindole.*

On treating the original syrupy residues, from which no further crystalline separation could be obtained during the crystallisation of the externally compensated base with the optically active acid, with caustic soda and purifying the liberated base by extraction with ether and distillation in the usual way, a mixture of *d*- and *l*-dihydro- $\alpha$ -methylindoles is obtained, in which the former predominates; it boils at  $225^{\circ}$ , and the samples prepared show the same gradual increase in rotatory power during the few hours succeeding the distillation as is observed with the *laevo*-base. Thus, one sample examined in a 1 dm. tube gave  $\alpha_D + 4.91^{\circ}$  one hour after distillation, but after the lapse of twelve hours the value had increased to  $\alpha_D + 5.60^{\circ}$ . This impure

dextro-base also corresponds with the pure lævo-base described above in that its rotatory power changes in sign in benzene solution. 1.415 grams of this sample of base, made up to 20 c.c. with benzene, gave  $\alpha_D - 0.50^\circ$  in a 2 dm. tube; whence  $[\alpha]_D - 3.6^\circ$ , and  $[M]_D - 4.7^\circ$ . *d*-Dihydro- $\alpha$ -methylindole has not yet been obtained in a state of purity.

*d-Benzoyldihydro- $\alpha$ -methylindole.*

On benzoylating the preceding impure dextro-base and crystallising the product from dilute alcohol, a sharp separation of the externally compensated and dextrorotatory benzoyl derivatives is readily effected. The optically active modification is much more sparingly soluble than the inactive substance, and the latter is therefore almost certainly not a racemic compound; this is the more probable because the excess of active component can be so easily separated by crystallisation. *d*-Benzoyldihydro- $\alpha$ -methylindole closely resembles its enantiomorphously related isomeride and melts at  $119^\circ$ .

0.1980 gave 0.1125  $H_2O$  and 0.5872  $CO_2$ .  $C = 80.88$ ;  $H = 6.31$ .

$C_{16}H_{15}ON$  requires  $C = 81.01$ ;  $H = 6.33$  per cent.

0.2916 gram, made up to 20 c.c. with absolute ethyl alcohol, gave  $\alpha_D + 1.08^\circ$  in a 3 dm. tube; whence  $[\alpha]_D + 37.03^\circ$  and  $[M]_D + 87.76^\circ$ . These values are arithmetically identical with those obtained with the lævo-isomeride.

*d-Acetyldihydro- $\alpha$ -methylindole.*

On acetylating the crude dextro-base, either with acetyl chloride or with acetic anhydride, and crystallising the product from light petroleum, a pure sample of *d*-acetyldihydro- $\alpha$ -methylindole is easily obtained; it crystallises in colourless needles melting at  $89^\circ$ .

0.2220 gave 0.1522  $H_2O$  and 0.6147  $CO_2$ .  $C = 75.52$ ;  $H = 7.61$ .

$C_{11}H_{13}ON$  requires  $C = 75.42$ ;  $H = 7.42$  per cent.

0.1745 gram, made up to 20 c.c. with absolute ethyl alcohol, gave  $\alpha_D + 1.04^\circ$  in a 2 dm. tube; whence  $[\alpha]_D + 59.6^\circ$  and  $[M]_D + 104.3^\circ$ . These numbers are in fair agreement with those obtained with the corresponding derivative of the lævo-base.

In order to ascertain that no optical inversion attends the formation of salts and acyl derivatives of the optically active dihydro  $\alpha$ -methylindoles, a quantity of the pure *d*-acetyldihydro- $\alpha$ -methylindole was boiled with 10 per cent. alcoholic potash until hydrolysis was complete; after acidification and evaporation, the base was liberated with caustic soda, extracted with ether, and benzoylated in the usual way. The benzoyl derivative thus obtained, after one crystallisation from a'cohol,

melted at  $119^{\circ}$  and gave the following results in a determination of rotatory power:

0.2436 gram, made up to 20 c.c. with absolute ethyl alcohol, gave  $\alpha_D + 0.89^{\circ}$  in a 2 dm. tube; whence  $[\alpha]_D + 36.5^{\circ}$  and  $[M]_D + 86.5^{\circ}$ . The dextro-base thus retains its optical activity throughout the series of operations involved in the hydrolysis of the acetyl derivative, the formation of a salt, the liberation of the base with caustic soda, and the preparation of the benzoyl derivative. The persistency with which the optical activity is retained is in striking contrast with the facility with which the optically active *ac*-tetrahydro- $\beta$ -naphthylamines undergo optical inversion (Pope and Harvey, Trans., 1901, 79, 74).

*Externally Compensated Benzoyldihydro- $\alpha$ -methylindole.*

It has been shown above that externally compensated benzoyldihydro- $\alpha$ -methylindole is almost certainly not a racemic compound. In order to complete the proof that a resolution of the parent base into its optically active components has been effected, it will suffice to show that on crystallising together equal weights of the pure *d*- and *l*-benzoyldihydro- $\alpha$ -methylindoles described above, an inactive benzoyl derivative, identical with that obtained on benzoylating the externally compensated base, is obtained. On crystallising a mixture in equal proportion of the two enantiomorphously related benzoyl derivatives from dilute alcohol, the inactive benzoyl compound melting at  $91-92^{\circ}$  is obtained; further, the melting point of the acyl derivatives thus produced is not depressed by adding to the substance a small quantity of benzoyl derivative prepared from the externally compensated base.\*

*The Sparingly Soluble Dihydro- $\alpha$ -methylindole d-Bromocamphorsulphonate.*

It has been shown above that on crystallising externally compensated dihydro- $\alpha$ -methylindole with *d*-bromocamphorsulphonic acid, a sparingly soluble *l*-dihydro- $\alpha$ -methylindole *d*-bromocamphorsulphonate separates first, then a salt melting at  $124-125^{\circ}$ , whilst *d*-dihydro- $\alpha$ -methylindole remains in the mother liquors; it would therefore naturally be assumed that the salt melting at  $124-125^{\circ}$  is *d*-dihydro- $\alpha$ -methylindole *d*-bromocamphorsulphonate. This, however, is not necessarily the case. After repeated crystallisation from ethyl acetate, the readily soluble

\* It may be remarked that the practice, which is now very generally adopted, of determining the identity or otherwise of two preparations by observing whether or not the melting point of either is depressed by the addition of a small quantity of the other substance, was first introduced by Kipping and Pope (Trans., 1893, 63, 548; 1895, 67, 371).

salt is obtained in nodular masses of colourless needles which melt sharply at 124—125°.

0.2840 gave 0.1560 H<sub>2</sub>O and 0.5342 CO<sub>2</sub>. C = 51.20; H = 6.10.

C<sub>19</sub>H<sub>26</sub>O<sub>4</sub>NBrS requires C = 51.35; H = 5.85 per cent.

The rotation constants are given by the following figures, which were obtained with separate fractions :

0.1505 gram, made up to 25 c.c. with water, gave  $\alpha_D + 0.658^\circ$  in a 2 dm. tube; whence  $[\alpha]_D + 54.6^\circ$  and  $[M]_D + 242.6^\circ$ .

0.2236 gram, made up to 25 c.c. with water, gave  $\alpha_D + 0.98^\circ$  in a 2 dm. tube; whence  $[\alpha]_D + 54.8^\circ$  and  $[M]_D + 243.2^\circ$ .

0.1117 gram, made up to 20 c.c. with water, gave  $\alpha_D + 0.61^\circ$  in a 2 dm. tube; whence  $[\alpha]_D + 54.6^\circ$  and  $[M]_D + 242.5^\circ$ .

The mean molecular rotatory power is thus  $[M]_D + 242.7^\circ$ , a value which indicates that the basic ion has a molecular rotatory power of the order  $[M]_D - 30^\circ$ ; this is incompatible with the demonstration given above that the basic ion in *l*-dihydro- $\alpha$ -methylindole *d*-bromocamphorsulphonate and hydrochloride has a molecular rotatory power considerably less than  $[M]_D + 10^\circ$ .

On treating a considerable quantity of the salt (2 grams) with a slight excess of caustic soda and extracting with benzene in exactly the same manner as described in connection with *l*-dihydro- $\alpha$ -methylindole *d*-bromocamphorsulphonate, a benzene solution is obtained which proves to be optically inactive when examined with a polarimeter capable of reading to 0.01°. Further, on benzoylating or acetylating either this inactive base or the salt from which it is derived, a pure sample of externally compensated benzoyl- or acetyl-dihydro- $\alpha$ -methylindole is at once obtained. Since it has been shown above that the *lævo*-base or its *d*-bromocamphorsulphonate invariably yields an optically active product as a result of such chemical changes as these, it is very remarkable that the salt having the molecular rotatory power  $[M]_D + 243^\circ$  yields only externally compensated base.

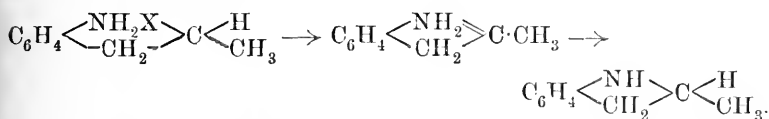
In the previous pages it is shown that on treating dihydro- $\alpha$ -methylindole with *d*-bromocamphorsulphonic acid, resolution proceeds normally in so far as concerns the formation of the salt melting at 179.5—180.5°, which yields the *lævo*-base, and the accumulation of the enantiomorphously related base in the mother liquors. An abnormality is observed, however, in the formation in considerable quantity of a salt melting at 124—125°; this salt has the molecular rotatory power  $[M]_D + 242.7^\circ$ , a number which differs greatly from the constant for the optically active ion which the salt contains, namely,  $[M]_D + 271^\circ$ , but yet does not yield an optically active base. The present case is very similar to those with which we have become

acquainted through the large amount of careful work done by Kipping on the resolution of hydrindamine and related bases, with the difference that, whilst we have only obtained evidence of the existence of three salts, two yielding active and one inactive base, this worker has prepared four isomeric salts all yielding optically active base. The proof of the formation of active or inactive base from our salts has been rendered simple by taking advantage of the fact that the rotation constants of an optically active base are usually greatly changed in magnitude by conversion into the benzoyl derivative; so that the almost negligibly small specific rotatory powers of the active dihydro- $\alpha$ -methylindoles become very large in the acyl derivative, and the presence of optically active base can therefore be readily ascertained.

In offering a provisional explanation of the occurrence of four isomeric salts during the resolution of hydrindamine and its derivatives, Kipping regards all four salts as of similar type. It would seem, however, that his  $\alpha$ -salts alone have the normal properties of the two salts, *d*-*B*, *d*-*A* and *l*-*B*, *d*-*A*, ordinarily separated when an externally compensated base, *d*-*B*, *l*-*B*, is treated with an optically active acid, *d*-*A*, in that their molecular rotatory powers are the sums of those of the basic and acidic ions into which they are resolved on solution in water; the law here involved has been confirmed in many cases of combination between powerful optically active acids and active bases, and the molecular weight determinations which Kipping has made (*Trans.*, 1903, 85, 944) in no way support his provisional assumption that the abnormal molecular rotatory powers of the  $\beta$ -salts are due to incomplete electrolytic dissociation. The  $\beta$ -salts thus differ from the  $\alpha$ -isomerides in exhibiting an abnormal, and at present unaccountable, molecular rotatory power; it therefore seems most reasonable to suppose that whilst the  $\alpha$ -salts have configurations and constitutions altogether in accordance with our present views, the  $\beta$ -salts are constitutionally peculiar in some manner which, as yet, we in no way understand.

The low molecular rotatory power of our salt melting at 124–125° arouses the suspicion that it contains a levorotatory basic ion, either pure or as a mixture in unequal proportions of compounds corresponding with Kipping's  $\beta l$ - and  $\beta l$ -salts. And, if so, the reason for its not yielding an active base or an active benzoyl derivative may be similar in kind to that advanced to explain the optical inversion of the *ac*-tetrahydro- $\beta$ -naphthylamines, namely, that in the salt melting at 124–125° the acidic group X is in such proximity to the hydrogen atom attached to the asymmetric carbon atom that on the liberation of the base these radicles H and X separate together, leaving the previously asymmetric carbon atom doubly bound to the nitrogen atom. Some such potentially inactive tautomeric modification of dihydro- $\alpha$ -methyl-

indole as that formulated below would thus be produced, and, in reverting to the normal form, would involve the optical inversion of the base, just as has been shown to occur in the case of the *ac*-tetrahydro- $\beta$ -naphthylamines.



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# CXXXVII.—*The Vapour Pressure of Sulphuric Acid Solutions and the Molecular Condition of Sulphuric Acid in Concentrated Solution.*

By BRYCE CHUDLEIGH BURT.

THIS work arose out of Prof. Campbell Brown's suggestion that a knowledge of the vapour pressures of concentrated sulphuric acid solutions would be of value, as possibly throwing light on some of the chemical changes taking place in the vitriol chambers and Glover tower.

It at once became evident that such results would be of wider interest as affording some insight into the molecular condition of sulphuric acid in solution, and on the nature of concentrated aqueous solutions. Despite the importance of the subject, but little work has been done in this direction, probably owing to the experimental obstacles to be overcome and the difficulty of interpreting the results obtained. Regnault (*Ann. Chim. Phys.*, 1845, [iii], 15, 179) gives the vapour pressure of sulphuric acid solutions for temperatures from 5° to 35°, and for concentrations ranging from 24.26 to 84.48 per cent.  $\text{H}_2\text{SO}_4$ .

Under these conditions it can be fairly assumed that what was measured was the lowered vapour pressure of the water present, the sulphuric acid being considered as a non-volatile substance. At higher temperatures, particularly with very concentrated solutions, the sulphuric acid itself may exert an appreciable vapour pressure, and at still higher temperatures the problem appears to be still further complicated by the dissociation of sulphuric acid into sulphur trioxide and water, even when as much as 30 per cent. of the latter is present.

Sorel (*J. Soc. Chem. Ind.*, 1890, 9, 175) has determined by the evaporation method the "vapour pressure of water vapour emitted from sulphuric acid solutions" up to 95°, and for concentrations up to 83 per cent.  $\text{H}_2\text{SO}_4$ . This method consisted in drawing an accurately measured volume of air through the sulphuric acid solution, maintained at constant temperature, and collecting the water vapour carried over. From the figures so obtained, the vapour pressure was calculated from the formula :

$$p = 6229 \frac{gT}{m(v + 6229gT/m\bar{b})}$$

where  $p$  = vapour pressure in mm. of mercury ;  $g$  = weight of vapour evolved ;  $v$  = volume of air ;  $m$  = molecular weight of vapour ;  $T$  = absolute temperature ;  $\bar{b}$  = barometric pressure.

The term  $6229gT/m\bar{b}$  is a correction for the volume of vapour carried over, and is the volume of vapour reduced to the same pressure as that under which the air was measured.

The limitations of the method are obvious. Should the sulphuric acid itself exert an appreciable vapour pressure, the results would not represent the vapour pressure of the aqueous vapour, neither would they indicate the total vapour pressure, since the vapour emitted would be of unknown composition. Moreover, owing to the small quantity of acid employed and the necessarily long duration of the experiment, the concentration of the acid becomes appreciably changed.

Briggs (*J. Soc. Chem. Ind.*, 1903, 22, 23), using the same method, has extended Sorel's determinations up to 200° for concentrations ranging to 91 per cent.  $\text{H}_2\text{SO}_4$ . The difficulties in Sorel's work are here increased, and the results are rendered still more uncertain by the difficulty of maintaining a constant temperature by the method employed.

In order to get over these difficulties, the author decided to measure the actual pressure under which the solutions boiled at different temperatures, thus measuring the total vapour pressure.

#### *Experimental Method.*

The method used throughout these determinations was the dynamical one. The liquid was boiled under various pressures and the temperature and pressure accurately registered. A modification of an apparatus designed by Innes for the determination of the molecular rise in boiling point for various benzene solutions under various pressures (Innes, *Trans.*, 1902, 81, 682) was employed.

The sulphuric acid solutions of known concentrations were boiled in the enlarged "Beckmann" tube, *A*, made of hard Jena glass, which had a stout platinum wire fused through the bottom and was partially

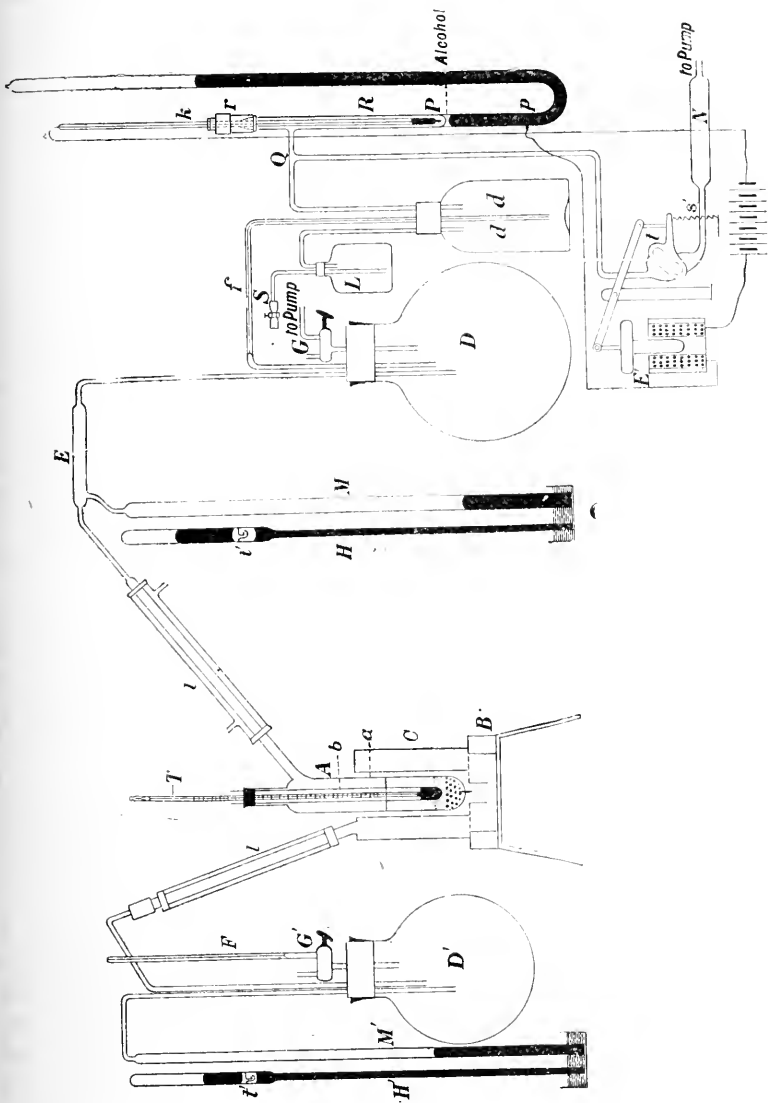


FIG. 1

filled with small glass beads mixed with platinum clippings. Under these conditions, even the most concentrated acids boiled quietly and regularly under pressures as low as 30 mm. of mercury. The tubes used were 4 to 4.5 cm. in diameter and 30 cm. long, the side-tube surrounded by a water condenser, *l*, being about 40 cm. in length. The outer end of this was connected in series by a short piece of thick-walled india-rubber tubing to the manometer, *M*, the drying tube, *E*, and the dead space, *D*. The experimental tube surrounded by the copper vapour-bath, *C*, was placed on the Beckmann asbestos air-bath, *B*, heated by a ring-burner, the tube itself being also heated by a small central flame.

The vapour-bath, *C*, made of stout copper and brazed absolutely vacuum tight, contained a liquid boiling under a known pressure, so adjusted that the temperature of the vapour was that of the experimental tube. The pressure in *C* was read by the second manometer and barometer, *M'H*. To prevent fluctuation in pressure, *C* was also connected to the large flask, *D'*, which served as dead space. By means of the three-way tap, *G'*, this reservoir could be connected either to the pump or could be opened to the atmosphere by means of the long capillary, *f*, which allowed of an accurate adjustment of the pressure. The liquids used were those recommended by Ramsay and Young (Trans., 1885, 47, 640): ethyl alcohol (40—70°), chlorobenzene (70—130°), bromobenzene (120—150°), aniline (150—180°), quinoline (180—235°).

The "dead space," *D*, simply serves to prevent any rapid fluctuation in pressure and consisted of a large stone jar of about 10 litres' capacity furnished with a tightly-fitting india-rubber bung. This was connected to the drying tube, *E*, and thence to the manometer and experimental tube. It is also connected by the capillary tube, *F*, to the smaller "dead space," *d*, which, in turn, was joined to the pressure regulator, *R*.

The latter, described by Innes (*loc. cit.*), consists of the siphon barometer, *R*, a stout platinum wire being fused through the short limb near to the bend. Though a piece of thick-walled india-rubber tubing at the upper end passes the tube, *k*, carrying the platinum point, *p*, electric contact with the wire being made by means of mercury. Connections are made with the electro-magnet, *E'*, and a six-cell storage battery, the former being so arranged that when the pressure in *R* rises, the circuit is broken and the tap *t* is opened by the spring *S'*, the tap being connected through the drying tube, *N*, to two vacuum water-pumps. The whole apparatus is thus momentarily connected to the pumps until the pressure is again reduced to the point required by the adjustment, when the circuit closes and the tap shuts. By this means, the whole apparatus could be maintained

under any desired pressure within less than 0.1 mm., the adjustment being made by sliding the tube, *k*, up or down, the final adjustment being made by means of the micrometer screw, *v*.

The capillary tube, *f*, was introduced to prevent any change of pressure in *d*, being rapidly followed by a fluctuation in the flask *D*. The latter vessel was fitted with a three-way tap, *G*, by which the apparatus could be connected either to the air or to the pumps in order to vary the pressure rapidly at the end of each determination. The natural leakage in the apparatus not being sufficient to keep the regulator working steadily, a small flask, *L*, containing a little strong sulphuric acid, was therefore connected to *d*, and a slow stream of air regulated by the screw clip, *S*, allowed to bubble through.

The pressure was adjusted until the liquid boiled at the desired temperature. Readings of pressure and temperature were taken for one to two hours to ensure steady boiling. The pressure was ascertained by means of the barometer and manometer, *H*<sub>1</sub>*M*<sub>1</sub>, placed over the same mercury reservoir. These were screwed to a wooden stand provided with a mirror glass scale accurately ruled in millimetres. By using a long focus lens, the mercury column and its image on the scale could be brought into coincidence, parallax error being thus avoided and the columns read with ease to 0.1 mm. The pressure so obtained was reduced to millimetres of mercury at 0°. Temperatures were read by means of two normal glass thermometers made by Goetze (Leipzig), graduated in tenths and filled with nitrogen under pressure, whilst temperatures below 100° were indicated by means of Hicks's standard thermometers. The thermometer was observed by means of a telescope, and thus read to 0.01°. When the mercury column projected beyond the tube, stem corrections were introduced, the stem temperatures being taken by Geissler's short range thermometers graduated in fifths. To avoid any straining of the bulb of the thermometer owing to the reduced pressure, the instrument was not placed directly in the liquid, but in the thin Jena glass tube, *b*, the bulb being surrounded with mercury.

The thermometers used were provided with auxiliary bulbs below the graduated stem, and below this were again graduated for a 1° range to enable the ice-point to be determined from time to time, thus guarding against any zero error. These instruments having been previously compared with the hydrogen scale by the Reichsanstalt, no further calibration was made.

The sulphuric acid used was supplied by Messrs. Towers, and was re-distilled from platinum. To prevent contamination, it was stored in sealed Jena flasks until required. A careful analysis showed it to be free from arsenic, lead, and iron, and it showed no evidence of the presence of nitrites by the brucine reaction.

The solutions used were prepared with distilled water, redistilled from lime, and free from carbon dioxide. These were made up only as required and kept in tightly-stoppered Jena flasks. Both the flasks and the experimental tubes were cleansed thoroughly with hot chromic acid and steamed out before use.

The strengths of the solutions were determined in duplicate by the gravimetric method, being also checked by titration with standard alkali and a specific gravity determination.

In all cases the concentration stated is the mean of at least two analyses agreeing within 0.02 per cent.

Concentrations are given throughout in parts of  $\text{H}_2\text{SO}_4$  per 100 parts of solution. Vapour pressure measurements were made for acids from 25 to 95 per cent., and for each interval of  $5^\circ$  from the boiling point under atmospheric pressure downwards. Each tabulated result is the mean of at least two concurrent determinations agreeing within 0.2 mm. The limit of working of the apparatus was about 30 mm., and no observations were made below this. In the case of the highest concentration, the determinations are made only up to  $230^\circ$ , since there was evidence that dissociation of the acid took place at this temperature into sulphur trioxide and water.

The molecular weight " $m$ " was calculated from Raoult's corrected formula:

$$\frac{p-p'}{p} = \frac{n}{n+N},$$

where  $p$  and  $p'$  are the vapour pressures of solvent and solution respectively,  $n$  the number of molecules of solute, and  $N$  the number of molecules of solvent.

This equation can be easily transposed into

$$m = M \cdot \frac{g}{G} \cdot \frac{p'}{p-p'},$$

where  $m$  = molecular weight of solute,  $M$  = molecular weight of solvent in the gaseous state,  $g$  = weight of solute present,  $G$  = weight of solvent present.

The values of  $m$  thus obtained are tabulated with the vapour pressures.

Regnault's values for the vapour pressures of water were used. The value of  $M$ , the molecular weight of the solvent, water, in the gaseous state, has been taken as 18. It is probable that this assumption is not justifiable in all cases, but in the present state of our knowledge no other course is open.

TABLE I.

<i>Series A.</i> 24·92 per cent. $\text{H}_2\text{SO}_4$ .			<i>Series B.</i> 30·46 per cent. $\text{H}_2\text{SO}_4$ .		
Temperature.	Vapour pressure.*	<i>m.</i>	Temperature.	Vapour pressure.	<i>m.</i>
55°	95·5	25·3	55°	86·8	22·8
60	120·7	25·5	60	111·0	23·1
65	153·7	27·5	65	140·6	23·8
70	192·7	28·3	70	176·6	24·5
75	240·2	29·5	75	219·8	25·2
80	295·1	29·5	80	271·3	25·6
85	363·3	31·0	85	332·8	25·6
90	439·1	30·3	90	403·4	26·0
95	532·6	31·4	95	488·2	26·5
100	640·8	32·1	100	589·9	27·4
104·80	759·6	32·2	107·11	762·7	28·5

\* Pressure is given throughout in mm. of mercury at 0°, but not corrected to sea-level. The value of *g* is 981·45.

<i>Series C.</i> 35·54 per cent. $\text{H}_2\text{SO}_4$ .			<i>Series D.</i> 41·01 per cent. $\text{H}_2\text{SO}_4$ .		
Temperature.	Vapour pressure.	<i>m.</i>	Temperature.	Vapour pressure.	<i>m.</i>
55°	78·2	19·7	60°	84·2	16·3
60	100·1	20·3	65	107·4	16·9
65	126·8	20·9	70	136·5	17·3
70	159·5	21·4	75	171·6	18·3
75	199·0	22·0	80	211·8	18·5
80	245·0	22·1	85	261·3	19·0
85	301·5	22·7	90	317·2	19·0
90	366·0	22·8	95	386·0	19·5
95	445·4	23·5	100	465·8	19·8
100	537·7	24·0	105	560·2	20·3
105	646·2	24·6	110	670·2	20·7
109·56	757·2	24·8	113·21	749·4	21·0

<i>Series E.</i> 48·37 per cent. $\text{H}_2\text{SO}_4$ .			<i>Series F.</i> 54·24 per cent. $\text{H}_2\text{SO}_4$ .		
Temperature.	Vapour pressure.	<i>m.</i>	Temperature.	Vapour pressure.	<i>m.</i>
60°	59·8	11·3	60°	44·1	8·98
65	79·0	12·3	65	57·3	9·42
70	100·4	12·7	70	74·0	9·91
75	126·4	13·1	75	94·1	10·3
80	157·8	13·5	80	118·1	10·6
85	195·9	13·9	85	146·4	10·9
90	241·2	14·3	90	182·9	11·4
95	293·5	14·6	95	223·8	11·6
100	355·6	14·9	100	267·4	11·6
105	429·8	15·2	105	325·5	12·0
110	515·4	15·5	110	391·9	12·2
115	621·9	16·2	115	470·9	12·6
120·82	754·0	16·4	120	561·8	12·9
			125	662·6	13·1
			128·7	753·7	13·4

*Series G.*62.81 per cent.  $\text{H}_2\text{SO}_4$ .

Temperature.	Vapour pressure.	<i>m.</i>
70°	35.4	5.44
75	45.9	5.75
80	58.0	5.94
85	73.6	6.23
90	92.3	6.48
95	115.8	6.80
100	140.0	6.87
105	171.5	7.08
110	210.8	7.40
115	255.3	7.66
120	308.0	7.92
125	368.5	8.15
130	433.3	8.37
135	517.6	8.57
140	612.8	8.83
145.85	745.0	9.23

*Series H.*70.78 per cent.  $\text{H}_2\text{SO}_4$ .

Temperature.	Vapour pressure.	<i>m.</i>
90°	35.5	3.16
95	44.8	3.32
100	57.0	3.49
105	71.0	3.72
110	89.0	3.95
115	—	—
120	140.4	4.53
125	171.3	4.75
130	205.2	4.90
135	246.3	5.10
140	291.2	5.23
145	355.4	5.60
150	426.9	5.90
155	501.5	6.09
160	589.0	6.32
166.47	740.05	6.82

*Series I.*74.36 per cent.  $\text{H}_2\text{SO}_4$ .

Temperature.	Vapour pressure.	<i>m.</i>
120°	80.8	2.99
125	99.5	3.16
130	120.4	3.30
135	146.9	3.47
140	178.4	3.82
145	221.0	3.91
150	260.7	4.10

*Series J.*77.26 per cent.  $\text{H}_2\text{SO}_4$ .

Temperature.	Vapour pressure.	<i>m.</i>
110°	35.1	2.06
115	44.8	2.24
120	56.1	2.40
125	69.3	2.52
130	85.5	2.69
135	105.1	2.86
140	127.7	3.01
145	156.4	3.22
150	188.9	3.40
155	229.7	3.64
160	273.9	3.82
165	326.6	4.04
170	387.1	4.25
175	454.3	4.44
180	525.7	4.58
185	610.8	4.77
189.87	748.3	5.28

*Series K.*78.50 per cent.  $\text{H}_2\text{SO}_4$ .

Temperature.	Vapour pressure.	<i>m.</i>
115°	37.7	2.01
120	47.7	2.17
125	58.2	2.27
130	71.8	2.40
135	87.4	2.53
140	108.0	2.72
145	133.2	2.93
150	163.7	3.15
155	196.3	3.32
160	235.2	3.50
165	276.8	3.64
170	329.8	3.85
175	385.7	4.01
180	445.8	4.13
185	520.2	4.31
190	597.2	4.44
195	689.6	4.61
198.35	756.8	4.71

*Series M.*85.14 per cent.  $\text{H}_2\text{SO}_4$ .

Temperature.	Vapour pressure.	<i>m.</i>
140°	31.5	1.21
145	39.6	1.32
150	51.3	1.50
155	63.4	1.62
160	77.6	1.75
165	94.1	1.87
170	115.0	2.02
175	137.9	2.16
180	164.2	2.29
185	194.1	2.42
190	227.9	2.55
195	269.5	2.68
200	307.4	2.88
205	361.3	2.96
210	424.6	3.15
215	495.2	3.34
220	577.8	3.54
225	670.3	3.75
228.55	752.9	3.96

*Series O.*88.4 per cent.  $\text{H}_2\text{SO}_4$ .

Temperature.	Vapour pressure.	<i>m.</i>
155°	31.8	1.07
160	38.9	1.16
165	48.5	1.27
170	59.4	1.38
175	72.4	1.50
180	87.3	1.60
185	102.3	1.68
190	120.5	1.77
195	145.2	1.9
200	171.5	2.04
205	205.3	2.20

*Series L.*81.15 per cent.  $\text{H}_2\text{SO}_4$ .

Temperature.	Vapour pressure.	<i>m.</i>
135°	52.8	1.78
140	65.3	1.91
145	82.6	2.10
150	101.7	2.26
155	124.6	2.44
160	150.4	2.59
165	180.9	2.75
170	218.9	2.95

*Series N.*86.61 per cent.  $\text{H}_2\text{SO}_4$ .

Temperature.	Vapour pressure.	<i>m.</i>
150°	37.7	1.23
160	57.7	1.45
165	71.2	1.57
170	87.3	1.71
175	105.6	1.84
180	126.6	1.96
185	150.4	2.08

*Series P.*91.01 per cent.  $\text{H}_2\text{SO}_4$ .

Temperature.	Vapour pressure.	<i>m.</i>
180°	45.5	1.10
185	55.6	1.21
190	67.9	1.31
195	82.2	1.43
200	98.1	1.54
205	115.9	1.64
210	138.2	1.77
215	163.2	1.90
220	190.3	2.02
225	223.6	2.16
230	263.5	2.32

Series Q. 95.94 per cent.  $\text{H}_2\text{SO}_4$ .

Temperature.	Vapour pressure.	m.
205°	34.1	1.12
210	40.8	1.22
215	50.1	1.35
220	60.8	1.49
225	72.2	1.61
230	85.9	1.75
235	106.0	—

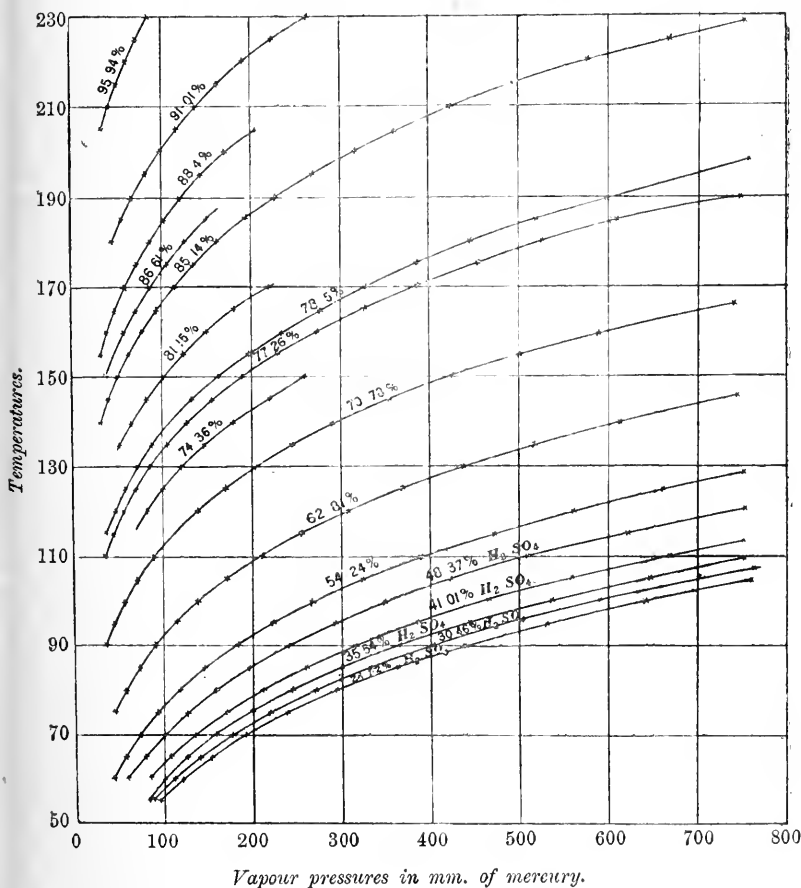
TABLE II.

Values of m calculated from Regnault's Vapour Pressure Measurements.

Concentration, $\text{H}_2\text{SO}_4$ per cent. solution.									
Temp.	24.26.	33.10.	37.6.	43.75.	52.13.	57.65.	64.47.	73.13..	84.48.
5°	30.7	18.97	19.10	13.77	9.56	6.09	4.98	3.11	1.59
6	31.08	—	—	—	—	—	—	—	—
7	31.15	—	—	—	—	—	—	—	—
8	31.22	—	—	—	—	—	—	—	—
9	31.24	—	—	—	—	—	—	—	—
10	31.15	21.02	19.01	13.87	9.72	6.37	4.94	2.84	1.24
11	—	—	—	13.87	—	—	—	—	—
12	—	—	—	13.87	—	—	—	—	—
13	—	—	—	13.88	—	—	—	—	—
14	—	—	—	13.88	—	—	—	—	—
15	30.19	21.77	18.67	13.88	9.77	6.55	4.88	2.66	1.02
16	—	21.80	—	—	—	—	—	—	—
17	—	21.82	—	—	—	—	—	—	—
18	—	21.81	—	—	—	—	—	—	—
19	—	21.78	—	—	—	—	—	—	—
20	29.0	21.74	18.35	13.91	9.82	6.70	4.84	2.53	0.88
25	28.13	21.42	18.17	14.03	9.96	6.88	4.82	2.46	0.77
26	—	—	18.15	—	—	—	4.82	—	—
27	—	—	18.15	—	—	—	4.82	—	—
28	—	—	18.14	—	—	—	4.83	—	—
29	—	—	18.14	—	—	—	4.83	—	—
30	27.93	21.09	18.20	14.29	10.06	7.02	4.83	2.43	0.70
31	27.99	—	—	—	—	—	—	2.43	—
32	28.07	—	—	—	—	—	—	2.43	—
33	28.2	—	—	—	—	—	—	2.43	—
34	28.3	—	—	—	—	—	—	2.43	—
35	28.59	20.75	18.56	14.74	10.32	7.24	4.88	2.44	0.66
Remarks.	Maximum at 9°. Minimum at 30°.	Maximum at 17°.	Minimum at 26°.	Stationary from 10° to 13°.			Minimum at 26°.	Stationary from 30° to 34°.	

*Discussion of Results.*

In calculating the molecular weights from Raoult's formula, the assumption has been made that the sulphuric acid itself exerts only a negligible vapour pressure. This is probably approximately true except at the highest temperatures, as is shown by the smoothness of

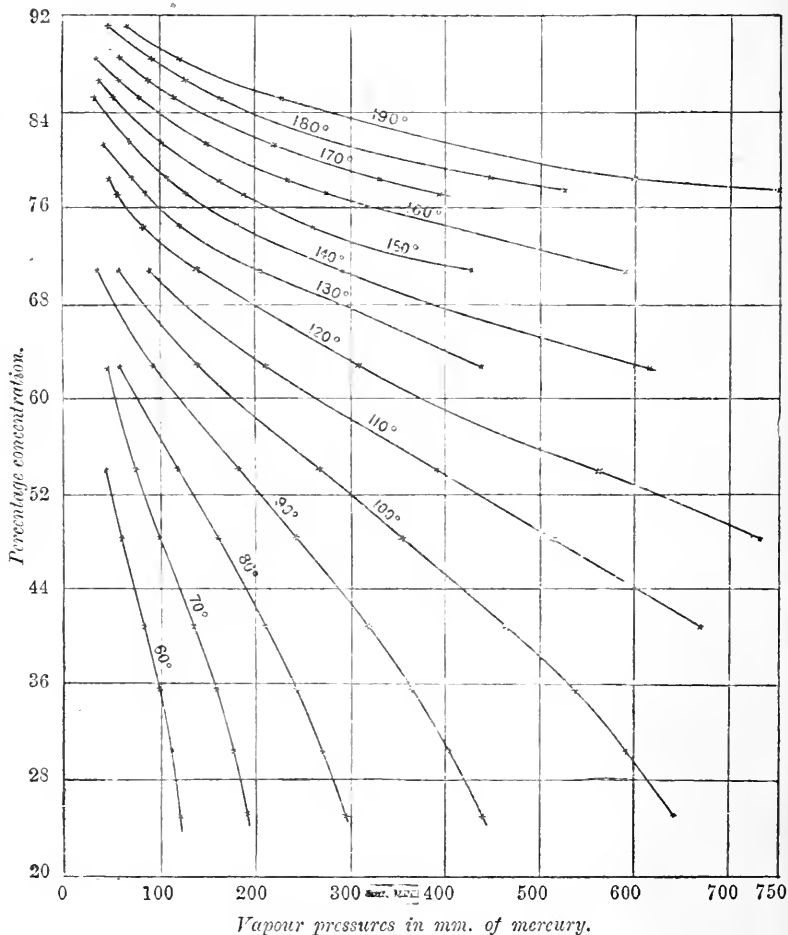
FIG. 2.—*Vapour pressures of sulphuric acid solutions. Isothermals.*

the vapour pressure curves and the fact that below 200° even 95 per cent. acid has an almost inappreciable vapour pressure. The additional, and less justifiable, assumption has necessarily been made, that the molecular weight of water in the gaseous state corresponds with the

simple formula  $H_2O$  over the whole range of temperature employed. In the absence of direct experimental data, this was unavoidable.

Before proceeding to the discussion of these results, it will be of interest to review briefly some of the earlier work on the subject.

FIG. 3.—Vapour pressures of sulphuric acid solutions. Isothermals.



It will be seen that the cryoscopic method has been almost exclusively employed.

Ponsot (*Compt. rend.*, 1896, 122, 668) found, on determining the molecular weight by the freezing point method, that this quantity decreased with increasing concentration to a minimum and then increased.

Dieterici (*Ann. Phys. Chem.*, 1897, [ii], 62, 616) found that for  $N/10$  to  $N$  solutions the molecular lowering decreased with increasing concentration.

Pickering (*Trans.*, 1890, 57, 64 and 331), from a study of the densities, heat of solution, conductivity, volume change on mixing, and expansion with heat for different solutions, concluded that 22 different hydrates exist in solution.

Linebarger (*Abstr.*, 1900, ii, 273), in describing an investigation by the surface-tension method, stated that the results pointed to the existence of extremely complex molecules.

Ramsay and Shields (*Trans.*, 1894, 65, 179), on investigating the surface-tension of a solution,  $12\text{H}_2\text{SO}_4, \text{H}_2\text{O}$ , of constant boiling point, obtained molecular weights from 32.3 to 2.8 times the normal for temperatures  $132.5^\circ$  to  $281^\circ$ . They concluded, moreover, that the decrease in molecular weight above  $132.5^\circ$  may be due either to the breaking up of complex molecules or to dissociation into sulphur trioxide and water.

Jones (*J. Amer. Chem. Soc.*, 1894, 16, 1), from a study of the lowering of the freezing point of acetic acid by a mixture of sulphuric acid and water compared with the values obtained when each was added alone, claims to have proved the existence of  $\text{H}_2\text{SO}_4, \text{H}_2\text{O}$  and  $\text{H}_2\text{SO}_4, 2\text{H}_2\text{O}$  in solution, but says that he was unable to obtain evidence of the existence of hydrates containing a greater proportion of water. These results were afterwards severely criticised by Pickering on the score of thermometric difficulties.

Pictet (*Compt. rend.*, 1894, 119, 642), by a cryoscopic method, found maxima and minima corresponding with definite hydrates,  $\text{H}_2\text{SO}_4$ ;  $\text{H}_2\text{SO}_4, \text{H}_2\text{O}$ ;  $\text{H}_2\text{SO}_4, 2\text{H}_2\text{O}$  and others down to  $\text{H}_2\text{SO}_4, 1000\text{H}_2\text{O}$ .

Lespieau (*Bull. Soc. chim.*, 1894, [iii], 11, 71), found that the monohydrate,  $\text{H}_2\text{SO}_4, \text{H}_2\text{O}$ , behaved cryoscopically as an individual.

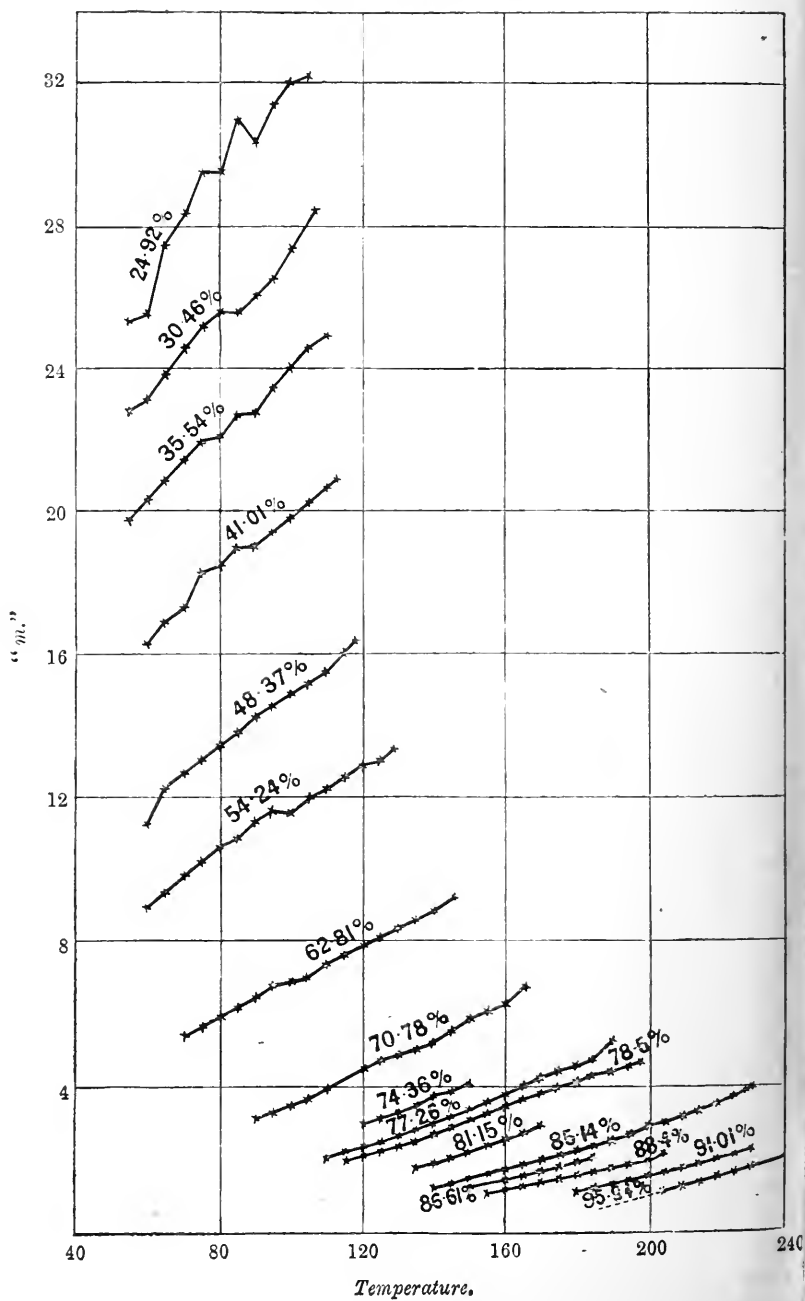
These results agree in the main with each other and also with those of the author in showing the tendency of sulphuric acid to form complexes with water when the latter is present as solvent.

The data obtained by Ramsay and Shields and also by Linebarger illustrate a different point, namely, the tendency of sulphuric acid to combine with itself to form complex molecules, in the presence of a little water.

It will be seen from Figs. 2 and 3 that the points, obtained when vapour pressure is plotted against temperature and concentration, lie on smooth curves, which are not, however, of any particular form, and do not fit any simple mathematical formula.

Such, however, is not the case when the calculated molecular weights are plotted against temperature and concentration, as will be seen from Figs. 4 and 5. These points lie on a series of short, straight

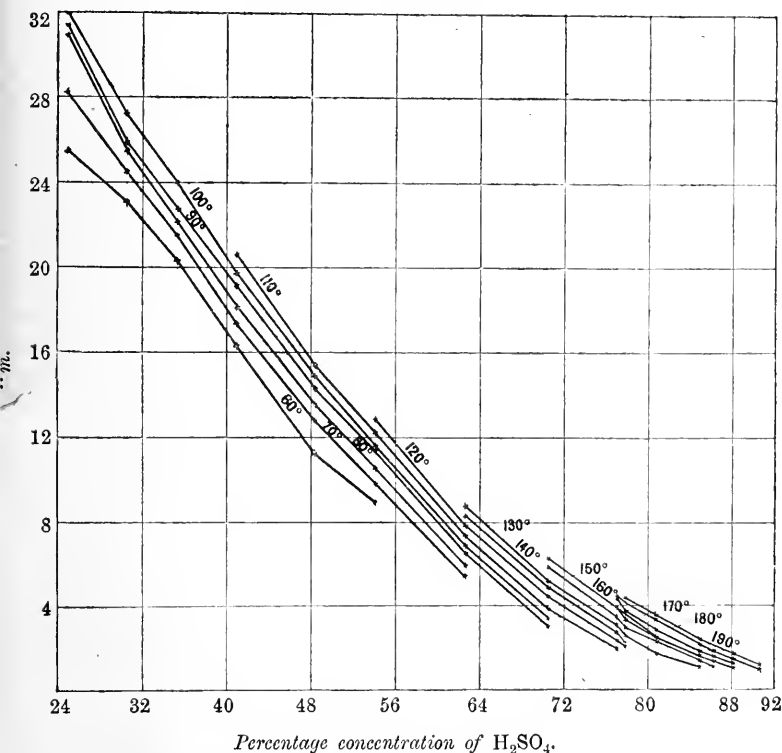
FIG. 4.—Influence of temperature on "m."



lines. It is not possible to draw continuous curves through them except in one or two cases, neither is it possible to fix on certain points as singular points or points of intersection of smooth curves. This result might be expected; it is perhaps too much to assume that Raoult's formula should apply to very concentrated solutions, even when the additional complicating factors, dissociation and combination with solvent, are absent.

From the figures themselves the following three inferences may be

FIG 5.—Influence of concentration on "m."



drawn: (i) In no case does the molecular weight calculated from these results rise above the value 32.7, which we should expect for  $H_2SO_4$ , completely dissociated into three ions.\* (ii) In most cases, it lies far below this, and, contrary to expectation, it decreases with concentration and increases with temperature. (iii) In the molecular weights calculated both from these and from Regnault's vapour pres-

\* It is evident, however, from the curves that it would rise above this value at lower concentrations and higher temperatures.

sure values (see Table II), we occasionally find inversion points in a series where the direction of the change with temperature is reversed as if some new factor became suddenly of increased importance. Moreover, these changes are most marked at the lower temperatures and concentrations, where no doubt as to the constitution of the vapour phase exists.

In the author's opinion these three facts clearly point to one conclusion, namely, that, in solution, combination ensues between sulphuric acid and water with the formation of new complexes. There is no evidence to show that definite hydrates exist in the solution; in fact, several attempts to calculate molecular weights, presupposing the existence of certain hydrates, led to very contradictory results.

The hypothesis, however, that such complexes exist, explains qualitatively at least the observed values of the molecular weight. It is at once evident that low values will be obtained; further, that as the concentration increases there will be an increased tendency for such complexes to form, and that the calculated molecular weight will decrease as the concentration increases. Also it is evident that as the temperature rises these complexes will tend to break up and the molecular weight will increase. It is possible that the question is further complicated by the electrolytic dissociation of these hydrates into ions other than  $2H^+$  and  $SO_4^{2-}$ . So far, conductivity and other measurements have thrown no light on the nature of the dissociation of sulphuric acid in concentrated solution. It is likely that the increased irregularity noticed with the more dilute solutions is due to the equilibria being further complicated by electrolytic dissociation.

It seems desirable that investigations should be extended to less concentrated solutions where the molecular weights obtained could be more easily compared with the values calculated from conductivity measurements. Also that the nature of other aqueous solutions should be investigated by this method, choosing a neutral substance as solute in order that the difficult problem of saturated solutions might be attacked under simpler conditions.

The author wishes to express his sense of indebtedness to Dr. W. Ross Innes for many kind suggestions with regard to the use of the apparatus, and to Professor Campbell Brown for the facilities he has afforded for the research and the kind interest he has taken in it throughout its progress.

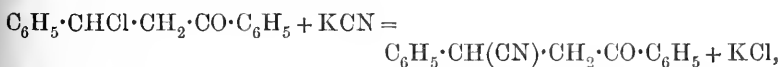
THE CHEMICAL LABORATORY,  
THE UNIVERSITY,  
LIVERPOOL.

CXXXVIII.—*Reactions Involving the Addition of Hydrogen Cyanide to Carbon Compounds. Part IV. Addition of Hydrogen Cyanide to Benzylideneacetophenone.*

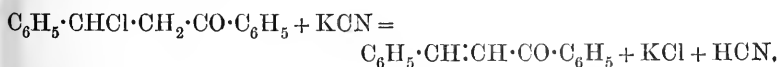
By ARCHIE CECIL OSBORN HANN and ARTHUR LAPWORTH.

IN continuation of the investigations on the addition of hydrogen cyanide to  $\alpha\beta$ -unsaturated ketones (this vol., p. 1214), we have examined a number of aromatic ketones with respect to their behaviour towards this agent under varied conditions. In no case was an interaction detected except when bases or metallic cyanides were present. Benzylideneacetone,  $C_6H_5 \cdot CH:CH \cdot CO \cdot CH_3$ , is rapidly altered by potassium cyanide, but the product, at least under all the conditions which we employed, is of a very mixed nature, and it is highly probable that the  $\beta$ -ketonitrile first formed very readily condenses with unaltered benzylideneacetone, yielding compounds of high molecular weight.

Benzylideneacetophenone, also, at first afforded us a mixed product, but of more attractive appearance, and it was not long before we were able to separate from this the expected additive product  $C_6H_5 \cdot CH(CN) \cdot CH_2 \cdot CO \cdot C_6H_5$ . This substance had previously been described by Anschütz and Montfort (*Annalen*, 1895, 284, 2) and independently by Rupe and Schneide (*Ber.*, 1895, 28, 960), and was obtained in both instances by acting on  $\beta$ -benzoyl- $\alpha$ -phenyl- $\alpha$ -chloroethane,  $C_6H_5 \cdot CHCl \cdot CH_2 \cdot CO \cdot C_6H_5$ , with potassium cyanide. This reaction is ostensibly expressed by the equation :



and Anschütz and Montfort regarded their observations as confirming the similar view which the former had previously advanced in explanation of the production of mesitonitrile from mesityl oxide hydrochloride (*loc. cit.*, p. 7). Rupe and Schneide, however, found that if the product is worked up immediately after the potassium chloride is formed, only benzylideneacetophenone can be isolated ; in consequence, they were led correctly to conclude that the kotonitrile is produced from the unsaturated ketone first formed and by addition of hydrogen cyanide thus set free :



Their remarks on their attempts to confirm their view are interesting :  
 "Diese Anlagerung von Blausäure ist um so auffallende da uns nie

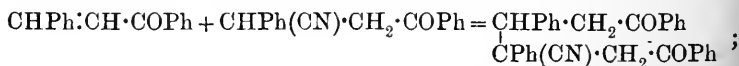
gelungen ist eine solche Addition an das einmal isolirtes Keton zu bewerkstelligen, indem wir auch hierüber eine Reihe von Versuchen angestellt haben. Allein wir erhielten auf diese Weise das Nitril ebenso wenig als wenn wir den Versuche dahin abänderten dass wir statt freie Blausäure, 2 mol. Cyankalium und die berechnete Menge Salzsäure anwendten. (Bei einen dieser letzten Versuche erhielten wir allerdings einmal einen neuen, schwer löslichen Körper, von welchem unten noch die Rede sein wird.)"

Our experiments, which were made before we were aware of previous work on the subject, serve to explain these observations, for we found that by adopting certain conditions described in the practical part of the paper a nearly quantitative yield of the cyanoketone may be obtained directly from benzylideneacetophenone. In brief, the important points are (1) that potassium cyanide must be present as well as free hydrocyanic acid, but (2) the salt must not exceed a certain concentration in comparison with that of the free acid, otherwise the alkalinity of the solution brings about a further change to which reference will shortly be made. No doubt when the chloroketone was treated with potassium cyanide in equimolecular proportion it was not entirely decomposed, so that enough of the salt was left to bring about the subsequent process of addition. In Rupe and Schneide's later experiments, the conditions adopted were such as to leave an insufficient quantity of potassium cyanide.

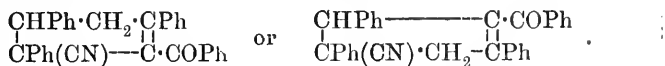
The sparingly soluble substance was analysed by Rupe and Schneide, who assigned to it the formula  $C_{31}H_{24}ON$ , and they regarded the substance as being formed by the interaction of two molecules of the unsaturated ketone with one molecule of hydrogen cyanide with the loss of an atom of oxygen; this formula was scarcely probable, however, unless it is assumed that the compound contains nitrogen with even valency. We find that the substance is produced when the concentration of potassium cyanide used is too high, and that it may also be obtained by allowing  $\beta$ -benzoyl- $\alpha$ -phenylpropionitrile—the initial product—to remain in solution with benzylideneacetophenone and alkali. Its true empirical formula is  $C_{31}H_{23}ON$ , and the compound may be represented as originating from the condensation of these components in equimolecular proportion, accompanied by loss of water,  $C_{15}H_{12}O + C_{16}H_{13}ON = C_{31}H_{23}ON + H_2O$ .

The probable explanation of its formation lies in the circumstance that the ketonitrile is a mono-substituted benzyl cyanide, which, like ethyl acetoacetate, condenses fairly readily with  $\alpha\beta$ -unsaturated ketones.

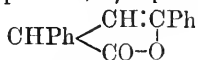
The process of addition would result in the change:



the product, like other 1:6-diketones, would readily lose water in alkaline solution to form a *cyclopentene* derivative,



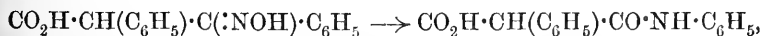
In harmony with this view, we find that the ketonitrile condenses with other  $\alpha\beta$ -unsaturated ketones and nitriles, yielding crystalline products.  $\beta$ -Benzoyl- $\alpha$ -phenylpropionic acid and its esters, as well as a triphenylpyridazinone formed by its interaction with phenylhydrazine, have been prepared by the previous workers, and in the main our results confirm theirs. Anschütz and Montfort (*Annalen*, 1895, 284, 5), on treating the acid with acetyl chloride, obtained, besides the normal dehydration product,  $\alpha\gamma$ -diphenylcrotonolactone,



(m. p.  $103^\circ$ ), a compound fusing at  $288^\circ$ , which they do not appear to have analysed. We find that the last-mentioned substance is formed from the acid under a variety of conditions, and is apparently isomeric with the foregoing lactone; it is perhaps the isomeric lactone,  $\text{CPh} \begin{array}{l} \swarrow \text{CH} \cdot \text{CHPh} \\ \searrow \text{CO} - \text{O} \end{array}$ , as it does not again yield the ketonic acid on hydrolysis, but gives rise to a very small quantity of an acid having the odour of phenylacetic acid.

The semicarbazide, the oxime, and *p*-nitrophenylhydrazone, are much more stable than the phenylhydrazone, and may be recrystallised from hot solvents apparently without alteration.

As the nitrile of the ketonic acid is formed, not by replacement of chlorine in the benzylideneacetophenone hydrochloride, but by addition of hydrogen cyanide to the unsaturated ketone, it was considered very desirable that a direct proof of the constitution of the acid should be obtained, and with this object we investigated the action of sulphuric acid on the oxime. The products were aniline and phenylsuccinic acid, which must clearly have arisen from the hydrolysis of phenylsuccinoanilic acid formed by the isomeric change of  $\beta$ -benzoyl- $\alpha$ -phenylpropionic acid oxime in the following manner:



a result which leaves no doubt as to the constitution of the ketonic acid.

The identification of the phenylsuccinic acid was rendered somewhat tedious owing to discrepancies between existing descriptions of its anhydride, the only very characteristic derivative of the acid which had previously been prepared. We were therefore compelled to pre-

pare the substance synthetically, and took the opportunity of characterising a number of its derivatives.

$\beta$ -Benzoyl- $\alpha$ -phenylpropionic acid,  $\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CH}(\text{C}_6\text{H}_5) \cdot \text{CO}_2\text{H}$ , contains an asymmetric carbon atom, and its resolution into the optical antipodes was therefore undertaken. It was converted into its quinine salt, which was fractionally crystallised from ethyl acetate and methyl alcohol, and from the fractions having the opposite extremes of solubility the dextro- and lævo-forms of the acid were finally isolated. The active forms are characterised by a marked tendency to form large crystals, and were obtained in beautiful, transparent plates or pyramids of considerable size, having  $[\alpha]_{\text{D}} + 157.3^\circ$  and  $[\alpha]_{\text{D}} - 157.6^\circ$  respectively in ethyl acetate under similar conditions. As these modifications were indistinguishable in crystallographic character from the inactive acid, it is highly probable that the latter is an inactive mixture and not a racemic compound, but unfortunately the quantity of active acid at our disposal was insufficient to allow us to confirm this.

#### EXPERIMENTAL.

##### *Addition of Hydrogen Cyanide to Benzylideneacetophenone.*

##### *Formation of $\beta$ -Benzoyl- $\alpha$ -phenylpropionitrile,* $\text{C}_6\text{H}_5 \cdot \text{CH}(\text{CN}) \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{C}_6\text{H}_5$ .

In the endeavour to bring about the union of hydrogen cyanide and benzylideneacetophenone, it was soon found that the action occurred quite readily in the cold when enough potassium cyanide was present, but in nearly all cases the product was a mixture, and contained the sparingly soluble substance mentioned by Rupe and Schneide (*loc. cit.*), as well as the desired additive compound. Later investigation showed that the former substance is produced by the interaction of the latter with the original unsaturated ketone, and was formed in all cases if the solution was too strongly alkaline; hence, by arranging that the solution contains a large amount of free hydrogen cyanide so as to diminish the hydrolytic dissociation of the salt, it became possible to prevent the occurrence of the secondary condensation. The following process for preparing the ketonitrile gives excellent results.

One molecular proportion of benzylideneacetophenone (23.4 grams) is dissolved in 450 c.c. of 92 per cent. alcohol at about  $35^\circ$ ; to this solution is added 6.9 grams (1 mol.) of glacial acetic acid and then 15 grams (2 mols.) of potassium cyanide dissolved in 45 c.c. of water, the latter addition being made gradually, while the whole is well shaken. In a few hours, a separation of small, scaly crystals takes place, and at the end of 24 hours the deposited matter, which

weighs 27 grams, may be removed by filtration, washed with water, and recrystallised from hot alcohol.

0.2000 gave 0.6000  $\text{CO}_2$  and 0.1020  $\text{H}_2\text{O}$ .  $\text{C} = 81.8$ ;  $\text{H} = 5.7$ .

0.5881 „ 25.67 c.c. nitrogen at  $15^\circ$  and 768.1 mm.  $\text{N} = 5.5$ .

$\text{C}_{16}\text{H}_{13}\text{ON}$  requires  $\text{C} = 81.7$ ;  $\text{H} = 5.5$ ;  $\text{N} = 5.9$  per cent.

This substance separates from alcohol in thin plates and from ethyl acetate in compact, transparent crystals, melting at  $126-127^\circ$ . It has all the properties of  $\beta$ -benzoyl- $\alpha$ -phenylpropionitrile.

The crystals from alcohol are well-formed, elongated, six-sided, orthorhombic plates, in which the extinction direction is coincident with the axis of greatest length; the acute bisectrix emerges through their apices, the axial plane being perpendicular to the large faces; the obtuse bisectrices thus emerge through the centre of the latter, as is seen when the crystals are examined in the usual way in convergent polarised light. The double refraction is moderate and negative in sign.

After fusion, the substance sets fairly quickly when cold, and, between glass slips, forms transparent or opalescent, sharply-defined needles arranged side by side, and shows very few air-spaces; these crystals appear crystallographically identical with those obtained from solution.

When the compound is boiled with solution of potassium or sodium hydroxide, it is somewhat rapidly decomposed, and the odour of acetophenone becomes perceptible; under certain conditions, also, hydrogen cyanide appears to be withdrawn as such, as was proved by the usual tests, but it cannot always be detected. The substance dissolves in strong sulphuric acid, and is precipitated nearly unchanged on the addition of water.

*Condensation of  $\beta$ -Benzoyl- $\alpha$ -phenylpropionitrile with Benzylideneacetophenone.*

The sparingly soluble compound, formed as a by-product in the preparation of the ketonitrile, was purified by repeated crystallisation from hot glacial acetic acid.

0.2020 gave 0.6468  $\text{CO}_2$  and 0.0998  $\text{H}_2\text{O}$ .  $\text{C} = 87.3$ ;  $\text{H} = 5.5$ .

0.7583 „ 22.55 c.c. nitrogen at  $19^\circ$  and 754.5 mm.  $\text{N} = 3.5$ .

$\text{C}_{31}\text{H}_{23}\text{ON}$  requires  $\text{C} = 87.5$ ;  $\text{H} = 5.4$ ;  $\text{N} = 3.3$  per cent.

As the composition of the substance was most easily explained on the assumption that it arose from the interaction of two molecules of benzylideneacetophenone with one of hydrogen cyanide, thus suggesting that benzoylphenylpropionitrile was an intermediate product, an

alcoholic solution of the nitrile was mixed with one of benzylidene acetophenone and made alkaline by the addition of a few drops of strong aqueous potassium hydroxide; a rapid separation of a crystalline solid occurred, and an excellent yield of the sparingly soluble compound referred to was obtained after half an hour's heating on the water-bath.

The compound is very sparingly soluble in the usual media, and has the properties ascribed to it by Rupe and Schneide (*loc. cit.*). It is best purified by crystallisation, first from nitrobenzene and afterwards from glacial acetic acid.

The crystals from nitrobenzene are small, rectangular plates with straight extinction, and probably belong to the orthorhombic system, and their directions of greatest length and elasticity are coincident, but their small size precludes further optical examination. After fusion between glass surfaces, the substance solidifies in a manner which varies greatly with the temperature. When quite cold, the material sets very slowly and imperfectly to minute, isolated needles; at higher temperatures, the solidification is more rapid, and fern-like, rhomboidal plates are formed, whilst near the melting point the substance sets quickly to compact, transparent plates.

When heated above its melting point, the compound quickly decomposes and darkens in colour, whilst hydrogen cyanide is evolved and an oily distillate is formed from which crystals of a comparatively fusible substance are deposited on cooling.

Attempts to convert the substance into a carboxylic acid were unsuccessful, as were all efforts to obtain any direct evidence as to its precise constitution.

$\beta$ -Benzoyl- $\alpha$ -phenylpropionitrile appears to be capable of condensing with other  $\alpha\beta$ -unsaturated ketones, and also with benzylidenbenzyl cyanide; the investigation of the products will be undertaken later.

*$\beta$ -Benzoyl- $\alpha$ -phenylpropionic Acid*,  $\text{C}_6\text{H}_5 \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{C}_6\text{H}_5$ .

In converting benzoylphenylpropionitrile into the corresponding acid, we sought for a more rapid method than that used by the previous workers, and finally adopted the following process as being the most satisfactory.

The nitrile is dissolved in five times its weight of strong sulphuric acid on the water-bath and the solution allowed to cool. Water is then added cautiously until a slight permanent precipitate is formed, when the liquid is heated to boiling in a reflux apparatus. A semi-transparent oil separates rapidly, and at the end of about one and a half hours the hydrolysis is complete, when the whole is allowed to cool and the acid liquid poured away from the solid cake of impure

ketonic acid. In order to purify the latter, it may be removed, ground to powder in a mortar, extracted with hot dilute sodium hydroxide, and the resulting aqueous solution of the sodium salt filtered and diluted largely with water. In recovering the acid from this solution, it is advisable to add to it, drop by drop, dilute acetic acid until a slight permanent precipitate is produced; this precipitate, at first oily, becomes crystalline after some little time, and the precipitation may be continued by the slow addition of dilute hydrochloric acid, when nearly the whole of the ketonic acid is obtained in a solid, pulverulent form. After separation at the filter-pump, the washed and dried material is recrystallised from a mixture of ether and light petroleum.

0.1976 gave 0.5451  $\text{CO}_2$  and 0.1004  $\text{H}_2\text{O}$ .  $\text{C} = 75.3$ ;  $\text{H} = 5.5$ .

$\text{C}_{16}\text{H}_{14}\text{O}_3$  requires  $\text{C} = 75.6$ ;  $\text{H} = 5.5$  per cent.

The equivalent was determined by titration with sodium hydroxide, employing phenolphthalein as indicator; 0.2993 required 11.85 c.c.  $N/10$   $\text{NaOH}$ , whence the equivalent = 252.3, the number calculated for a monobasic acid,  $\text{C}_{16}\text{H}_{14}\text{O}_3$ , being 254.

$\beta$ -Benzoyl- $\alpha$ -phenylpropionic acid separates from a mixture of chloroform or ether and light petroleum in small, glistening plates, and is deposited from hot ethyl acetate in small, compact, transparent tablets melting at  $152$ — $153^\circ$ .

The plate-like crystals, examined in polarised light, show straight extinction, and their planes are parallel to the plane of the optic axes. Fragments of the more compact crystals, examined in cedar-wood oil in convergent polarised light, show occasionally the interference figure corresponding with the bisectrix of a biaxial crystal of moderately wide axial angle; the double refraction is moderate and positive in sign.

When fused between glass slips, the acid solidifies very slowly and imperfectly, when cool, to aggregates of parallel, flat needles, through each of which the acute bisectrix emerges perpendicularly, or nearly so; in all probability, these needles are crystallographically identical with the above described plates.

The substance dissolves readily in pure strong sulphuric acid forming a colourless solution, from which it is reprecipitated by water practically unchanged; if, however, the sulphuric acid contains traces of nitric acid or nitrous fumes, the resulting solution is claret-coloured, but becomes colourless on dilution (Anschütz and Montfort, *Annalen*, 1895, 284, 3). Long-continued heating with moderately strong sulphuric acid causes the partial conversion of the substance into the anhydro-compound described later.

Of the sparingly soluble salts which have not before been described, the *mercuric* salt is white and microcrystalline; the *cobalt* and *nickel* salts are apparently amorphous, and are pink and green respectively.

Anschütz and Montfort describe an anhydride of  $\beta$ -benzoyl- $\alpha$ -phenylpropionic acid, which they prepared by heating the latter with acetyl chloride; this was accompanied by another substance, melting at  $288^\circ$ , which they do not appear to have analysed (*loc. cit.*, p. 5). We have obtained the less fusible compound by other methods, and find that it is apparently isomeric with the anhydride fusing at  $103^\circ$ .

When the ketonic acid is heated at  $120$ – $130^\circ$ , it gradually diminishes in weight owing to loss of water, and at the end of some hours the residue, if extracted with dilute alkali, is found to contain a neutral substance, which melts above  $280^\circ$  and is identical with the compound mentioned by Anschütz and Montfort. A more convenient method of producing the material was discovered accidentally as the result of an experiment on the hydrolysis of the ketonitrile with diluted sulphuric acid when the heating was continued for several hours longer than was subsequently found necessary in preparing the ketonic acid; the product was only partially dissolved by aqueous alkalis, and the insoluble portion, after crystallisation from nitrobenzene, melted at  $284$ – $286^\circ$ .

$\beta$ -Benzoyl- $\alpha$ -phenylpropionic acid also yields this anhydro-compound when heated on the water-bath with strong sulphuric acid for two hours, but in this case the greater part of the material used is not precipitated on addition of water, and probably undergoes sulphonation.

A specimen of the compound, prepared by heating the ketonitrile with sulphuric acid, was analysed, after recrystallisation from nitrobenzene.

0.2050 gave 0.6138  $\text{CO}_2$  and 0.0925  $\text{H}_2\text{O}$ .  $\text{C} = 81.7$ ;  $\text{H} = 5.0$ .

$\text{C}_{16}\text{H}_{12}\text{O}_2$  requires  $\text{C} = 81.3$ ;  $\text{H} = 5.0$  per cent.

The compound is very sparingly soluble in all the ordinary media, but dissolves somewhat freely in boiling nitrobenzene, from which it separates on cooling in small crystals, which fuse at  $284$ – $286^\circ$ , and we have never been able to observe a sharp melting point or to attain the number given by Anschütz and Montfort (*loc. cit.*).

The crystals are minute, slender needles, which in polarised light extinguish in directions which vary considerably with the orientation, but the individuals were too small to allow of fuller examination. When heated in small quantities, the substance sublimes to some extent before melting, and, when the experiment is made on an ordinary microscope slide, partial decomposition occurs during the rather long period required to fuse the whole completely, and the mass does not afterwards resolidify.

Although this substance appears to be isomeric with the more fusible anhydride, we have been unable to regenerate benzoylphenyl-

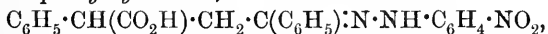
propionic acid from it. It is altered only very slowly by hot alcoholic potassium hydroxide, owing in part, no doubt, to its very sparing solubility in alcohol; if, after many hours' heating, the liquid is diluted with water, resinous products are precipitated; the supernatant aqueous liquid affords a precipitate on addition of mineral acid, but this was afterwards only partially soluble in dilute sodium carbonate, and its properties suggested those of a phenol rather than of a carboxylic acid. The small portion which dissolves in sodium carbonate is somewhat volatile in steam and has the odour of phenylacetic acid.

By the action of phenylhydrazine on benzoylphenylpropionic acid in the cold, Anschütz and Montfort obtained a substance which had the composition of an additive product of the components and melted and decomposed at  $85^{\circ}$  (*loc. cit.*, p. 6). On repeating this experiment, we observed the formation of the compound they describe, and succeeded in recrystallising it from methyl alcohol and from ethyl acetate, when in both cases the purified material melted and evolved gas, but without darkening appreciably, at  $112-115^{\circ}$ ; it crystallised in excessively slender needles which have straight extinction in polarised light. If recrystallised from hot alcohol or from hot glacial acid, it is converted into 1:3:5-triphenylpyridazinone, which is also obtained when a mixture of phenylhydrazine and benzoylphenylpropionic acid are heated together in alcohol or in acetic acid (Anschütz and Montfort, *loc. cit.*, p. 6).

1:3:5-Triphenylpyridazinone melts at  $122-123^{\circ}$  and separates from glacial acetic acid in transparent, rectangular plates or flat needles belonging in all probability to the orthorhombic system; the acute bisectrix emerges perpendicularly through the large faces. The axial angle is very small, and the double refraction, which is weak, is positive in sign.

The ketonic character of  $\beta$ -benzoyl- $\alpha$ -phenylpropionic acid was confirmed by preparing from it the following characteristic derivatives.

The *p*-nitrophenylhydrazone,



was made by heating the acid with *p*-nitrophenylhydrazine in glacial acetic acid on the water-bath for some hours. On diluting the solution with water, an oil was precipitated which finally solidified and was purified by crystallisation from hot glacial acetic acid.

0.2056 gave 0.5117  $\text{CO}_2$  and 0.0940  $\text{H}_2\text{O}$ .  $\text{C} = 67.8$ ;  $\text{H} = 5.0$ .

$\text{C}_{22}\text{H}_{19}\text{O}_4\text{N}_3$  requires  $\text{C} = 67.8$ ;  $\text{H} = 4.9$  per cent.

This compound is only sparingly soluble in the ordinary organic media; it separates from hot glacial acetic acid as a yellow powder, which under the microscope is seen to consist of small, slender, yellow needles melting sharply at  $188-189^{\circ}$ .

The *semicarbazone*,  $C_6H_5 \cdot CH(CO_2H) \cdot CH_2 \cdot C(C_6H_5) : N_2H \cdot CO \cdot NH_2$ , was made by dissolving the ketonic acid in the smallest quantity of dilute sodium hydroxide and warming the solution with excess of semicarbazide. The product was slowly deposited as a white powder which was collected, washed, and crystallised from absolute alcohol. A specimen dried in a vacuum over sulphuric acid was analysed:

0.2039 gave 0.4924  $CO_2$  and 0.1027  $H_2O$ .  $C = 65.8$ ;  $H = 5.6$ .

$C_{17}H_{17}O_3N_3$  requires  $C = 65.6$ ;  $H = 5.5$  per cent.

The semicarbazone is nearly insoluble in light petroleum, chloroform, benzene, and cold ethyl acetate, or acetone and is only sparingly soluble in the two last-named solvents at their boiling points; it dissolves readily, however, in hot glacial acetic acid, and does not separate from the solution on cooling, but may be recovered by dilution with water. It is best crystallised from boiling absolute alcohol, from which it is deposited as a white powder, melting at  $189-191^\circ$ .

The crystals from dilute acetic acid are small, probably orthorhombic, six-sided plates, which generally have curved edges; the crystals from alcohol are similar, but have straight sides. The double refraction is weak.

The *oxime*,  $C_6H_5 \cdot CH(CO_2H) \cdot CH_2 \cdot C(C_6H_5) : N \cdot OH$ , was made by adding a strong solution of sodium hydroxide ( $2\frac{1}{2}$  mols.) to a mixture of benzoylphenylpropionic acid (1 mol.) and hydroxylamine hydrochloride ( $1\frac{1}{2}$  mols.) and warming the resulting liquid for some hours on the water-bath. The liquid was then diluted largely with water and the oxime precipitated by the cautious addition of dilute hydrochloric acid. When the latter process is carried out skilfully, the product is white and pulverulent, and may be removed by filtration, dried, crystallised from benzene, and being finally exposed for some hours in a desiccator over sulphuric acid.

0.2038 gave 0.5681  $CO_2$  and 0.1108  $H_2O$ .  $C = 76.0$ ;  $H = 6.0$ .

$C_{16}H_{15}O_3N$ ,  $C_6H_6$  requires  $C = 76.1$ ;  $H = 6.1$  per cent.

The analysis indicated that the material contained a molecular proportion of benzene of crystallisation, and to confirm this a portion of the substance was warmed in a test-tube, when the benzene evolved was detected by the customary tests.

The crystals are very narrow, rhomboidal or diamond-shaped plates, which in polarised light extinguish obliquely to both pairs of sides; heated quickly, they melt at  $83^\circ$ , and completely fuse at  $87^\circ$ . The compound is readily soluble in all the usual organic media with the exception of light petroleum, but does not crystallise very satisfactorily from any of the ordinary solvents except benzene, but a specimen deposited from methyl alcohol was microcrystalline, melted

fairly sharply at 130—132°, and did not resolidify even after some days. When heated at 100°, it slowly diminishes in weight, possibly owing to its conversion into an ortho-oxazine compound after the manner of oximes of other  $\gamma$ -ketonic acids.

*Action of Sulphuric Acid on the Oxime of  $\beta$ -Benzoyl- $\alpha$ -phenylpropionic Acid.*

The carefully purified oxime was dissolved in five times its weight of 95 per cent. sulphuric acid and the solution warmed on the water-bath for 5 minutes, when the light brown liquid was cooled and poured into twice its bulk of water. A viscid, yellow mass separated, but no attempt was made to isolate the anilide which was presumably present, but the whole product heated to boiling until the greater part of the insoluble material had disappeared; a slight excess of alkali was then added and the aniline produced removed by distillation in steam. The alkaline liquid remaining in the distilling flask was then acidified with hydrochloric acid, evaporated to dryness on the water-bath, and the residue extracted with ethyl acetate, from which, on evaporation, a viscid mass was obtained; this was as far as possible dissolved in dilute ammonia, the solution boiled with animal charcoal until neutral to litmus paper, when it was filtered and mixed with a boiling concentrated solution of calcium chloride. The white salt which separated was removed, washed, and decomposed with a little warm hydrochloric acid, and the liberated acid purified by repeated crystallisation from water and dried over sulphuric acid.

0.2312 gave 0.5261  $\text{CO}_2$  and 0.1095  $\text{H}_2\text{O}$ .  $\text{C} = 62.1$ ;  $\text{H} = 5.3$ .

$\text{C}_{10}\text{H}_{10}\text{O}_4$  requires  $\text{C} = 61.9$ ;  $\text{H} = 5.2$  per cent.

The substance has the general properties attributed to phenylsuccinic acid, and was sparingly soluble in cold water, but dissolved readily on boiling, and was deposited from the solution on cooling in aggregates of fine needles, which in polarised light had straight extinction, and in which the directions of greatest elasticity and length were coincident. It melted at 166—167°.

In order to obtain further confirmation of the identity of the acid, it was warmed with excess of acetyl chloride until dissolved, the solution being then evaporated to dryness, the residue exposed over potassium hydroxide in a vacuum, and then extracted repeatedly with carbon disulphide, with the result that it was deposited from the solution on spontaneous evaporation in flat needles, which were collected and recrystallised from a mixture of ethyl bromide and light petroleum.

0.1881 gave 0.4679  $\text{CO}_2$  and 0.0758  $\text{H}_2\text{O}$ .  $\text{C} = 67.9$ ;  $\text{H} = 4.5$ .

$\text{C}_{10}\text{H}_8\text{O}_3$  requires  $\text{C} = 68.2$ ;  $\text{H} = 4.5$  per cent.

The compound has the general character of an anhydride. It crystallises in needles having straight extinction and with their directions of greatest elasticity and length at right angles. In the majority of cases, when these crystals are examined in the usual way in convergent polarised light, an axis of a biaxial interference figure is perceived to emerge obliquely through the large face; the axial plane is perpendicular to the direction of greatest length; the double refraction is strong.

After fusion, the substance solidified very slowly to an opaque mass of minute needles embedded in a transparent magma; the compound so obtained had a definite melting point at  $53\text{--}54^\circ$ .

Bredt and Kallen, however, who prepared phenylsuccinic acid by a different process, give the melting point of the anhydride as  $150^\circ$  (*Annalen*, 1896, 293, 349) and attribute the low melting point previously obtained to impurities; as these authors analysed the substance they describe, and also determined the amount of alkali required to neutralise the acid produced by hydrolysis of a known weight of anhydride, obtaining numbers apparently confirming this view, we were compelled to synthesise phenylsuccinic acid by a process which left no doubt as to the composition of the product, in order to ascertain the true melting point of its anhydride.

The method adopted was that of Spiegel (*Annalen*, 1883, 219, 31), which consists in condensing ethyl  $\alpha$ -bromo-(or chloro-)-phenylacetate with ethyl sodiomalonate in absolute alcohol. The product, ethyl carboxyphenylsuccinate, solidified readily, and was recrystallised, decomposed by strong aqueous potassium hydroxide, and the resulting tricarboxylic acid,  $\text{C}_6\text{H}_5\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}(\text{CO}_2\text{H})_2$ , heated so as to cause its decomposition into carbon dioxide and phenylsuccinic acid. The latter, after purification by means of the calcium salt, was converted into the anhydride by two methods, firstly by the foregoing process, and secondly by Bredt and Kallen's method, which consisted in heating the acid alone. The specimens in both cases had all the properties of the substance obtained from the oxime, and melted sharply at  $53\text{--}54^\circ$ .

A specimen made by heating phenylsuccinic acid was analysed:

0.2068 gave 0.5162  $\text{CO}_2$  and 0.0866  $\text{H}_2\text{O}$ .  $\text{C} = 68.1$ ;  $\text{H} = 4.7$ .

$\text{C}_{10}\text{H}_8\text{O}_3$  requires  $\text{C} = 68.2$ ;  $\text{H} = 4.5$  per cent.

In confirmation, 0.5547 gram of the anhydride was heated with water until dissolved; the solution required 63.5 c.c.  $N/10$  NaOH for neutralisation. The equivalent of the compound was therefore 87.4, the calculated number being 88 for phenylsuccinic anhydride and 97 for the acid itself.

The product was therefore phenylsuccinic anhydride, and had all the characters of a pure substance. It was observed, however, that when it was exposed to the atmosphere of the laboratory for several days the glistening, transparent crystals became dull and opaque, and the melting point became less sharp, until after some weeks it had nearly the same melting point as phenylsuccinic acid, but it then dissolved readily in cold dilute sodium carbonate. Having accumulated some quantity of the pure anhydride, it was thought worth while to prepare some other derivatives of phenylsuccinic acid, in order more fully to characterise the substance.

*Phenylsuccinanilic acid*,  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CH}(\text{C}_6\text{H}_5)\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$ , was made by mixing solutions of equimolecular proportions of the anhydride and pure aniline in benzene and warming the whole on the water-bath; the crystalline material which separated was collected, dried, and crystallised from ethyl acetate. In order to ascertain whether the product was the desired anilic acid, it was titrated with standard sodium hydroxide; 0.2304 gram required 8.65 c.c. *N*/10 NaOH, whence the equivalent = 266.3, the calculated value being 269.

The substance is soluble in cold aqueous sodium carbonate and is reprecipitated on the addition of hydrochloric acid. It dissolves sparingly in cold alcohol and ethyl acetate, readily in acetone, and is nearly insoluble in cold chloroform, benzene, and light petroleum. It melts at  $170-171^\circ$ ; the crystals from ethyl acetate are obliquely truncated flat needles, having straight extinction in polarised light, and the directions of greatest elasticity and length are at right angles.

When heated above its melting point, this compound is slowly converted, by loss of water, into *phenylsuccinanil*,  $\begin{array}{c} \text{CH}(\text{C}_6\text{H}_5) \\ | \\ \text{CH}_2-\text{CO} \end{array} > \text{N}\cdot\text{C}_6\text{H}_5$ ,

which is best prepared by distillation and subsequent crystallisation, first from benzene and then from ethyl acetate. It dissolves readily in alcohol, chloroform, and acetone, but is only sparingly soluble in light petroleum, and does not dissolve in warm dilute sodium hydroxide. It melts at  $137-138^\circ$ ; the crystals are thin, flat needles having straight extinction in polarised light. After fusion between glass slips, they solidify suddenly and completely on cooling to oval patches of concentrically-arranged slender needles.

*Phenylsuccino-p-tolil*,  $\begin{array}{c} \text{CH}(\text{C}_6\text{H}_5) \\ | \\ \text{CH}_2-\text{CO} \end{array} > \text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_3$ , was prepared in a similar manner from phenylsuccinic anhydride and *p*-toluidine, and is the most characteristic derivative which we have examined. In general properties, it resembles the preceding substance, but it crystallises from benzene in beautiful, glistening, flat needles of considerable size, and melts at  $138-139^\circ$ .

When fused on a microscopic slide beneath a cover-slip, it solidifies

rapidly on cooling to a nearly transparent mass of well-formed flat needles, which, when examined in polarised light, are seen to be biaxial in character, and a bisectrix of an interference figure of very wide angle emerges normally to the field in most cases. If this is the obtuse bisectrix, as is probably the case, the double refraction is negative.

*Resolution of  $\beta$ -Benzoyl- $\alpha$ -phenylpropionic Acid into its Optical Isomerides.*

*d- and l- $\beta$ -Benzoyl- $\alpha$ -phenylpropionic Acids.*

Examination of a number of salts of the ketonic acid with various optically active bases indicated that the quinine salt would probably be the most easily dealt with, as it was somewhat sparingly soluble in ethyl acetate and crystallised readily.

Molecular proportions of the inactive acid and quinine were therefore dissolved in a considerable bulk of ethyl acetate, the two solutions were mixed, and the solid which separated was removed and recrystallised repeatedly from methyl alcohol, in which it was somewhat freely soluble, and afterwards from ethyl acetate. The alcoholic mother-liquors on partial evaporation afforded a salt having much the appearance of the more highly purified material, and this was therefore collected and recrystallised from ethyl acetate until its rotatory power was nearly constant. The fractions which had a rotatory power between  $[\alpha]_D - 60^\circ$  and  $-70^\circ$  were united, and the crystallisation from ethyl acetate recommenced. It was found that a slight further change in rotatory power occurred after each recrystallisation, and it was suspected that this was due, not to incomplete resolution, but to slight changes in the composition of the salt.

For the determination of the rotatory value of the most highly purified salt, 0.397 gram in absolute alcohol (25 c.c.) was examined in a 2 dm. tube, and had  $\alpha_D - 1.92^\circ$ , whence  $[\alpha]_D - 60.4^\circ$ .

The material was transferred to a separating funnel with ethyl acetate and a little water, the whole being shaken repeatedly with small successive quantities of dilute sodium hydroxide, the aqueous portions being united and acidified with dilute hydrochloric acid. The resulting precipitate was well washed with water, dried, and crystallised from ethyl acetate.

0.2500 gram of the acid thus obtained was dissolved in ethyl acetate (14.95 c.c.) and the resulting solution examined in a 2 dm. tube; it had  $\alpha_D + 5.26^\circ$  whence  $[\alpha]_D + 157.3^\circ$ .

0.2039 gave 0.5648  $\text{CO}_2$  and 0.1026  $\text{H}_2\text{O}$ .  $\text{C} = 75.5$ ;  $\text{H} = 5.6$ .

$\text{C}_{16}\text{H}_{14}\text{O}_3$  requires  $\text{C} = 75.6$ ;  $\text{H} = 5.5$  per cent.

*d*- $\beta$ -Benzoyl- $\alpha$ -phenylpropionic acid crystallises in much more characteristic forms than does the inactive acid, and separates from ether in beautiful, transparent, glassy plates melting at 176—178°.

The crystals probably belong to the orthorhombic system and show the forms {100}, {011}, {010}, and {001}; the first is the most strongly developed and is parallel to the axial plane. Crushed fragments examined in cedar-wood oil in convergent polarised light show, here and there, the figure corresponding with the acute bisectrix of a crystal of moderate axial angle; the double refraction is moderately large and positive in sign. When fused between glass slips, it solidifies rapidly in masses of long, flat, parallel needles, with very few air-spaces, and the acute bisectrix of these, which are apparently crystallographically identical with the foregoing plates, is perpendicular to their common plane.

Apart from the greater facility of crystallisation exhibited by the active acid, it is apparently crystallographically identical with the inactive acid previously described, so that the latter is probably not racemic in character.

The *semicarbazone* of *d*- $\beta$ -benzoyl- $\alpha$ -phenylpropionic acid, made by the usual method and purified by crystallisation from hot methyl alcohol, was readily soluble in all the ordinary media with the exception of water and light petroleum. When heated slowly, it changed in appearance and melted at 107—110°, and at 120° had become transparent, although solid; on raising the temperature further, it softened and slowly evolved gas at about 160°, and finally liquefied without any appreciable darkening.

The crystals are flat needles which, in polarised light, extinguish at about 14° to their edges, and their elasticity was less in the direction of greatest length than at right angles to it.

*l*- $\beta$ -Benzoyl- $\alpha$ -phenylpropionic Acid.—As it was suspected from the behaviour of the more sparingly soluble quinine salt that the resolution had been fairly efficient after the first separation of solid, the initial ethyl acetate mother-liquors from the preparation of *l*-quinine *d*-phenacyl- $\alpha$ -toluate were extracted by shaking with dilute sodium hydroxide, the acid being precipitated by addition of hydrochloric acid. The solid product was purified by reconversion into sodium salt, precipitated by mineral acid, washed, and dried. The acid thus obtained was crystallised from purified ether and separated at once in large plates exactly resembling those of the *d*-acid. After another crystallisation from ether, its rotatory power was determined. 0.2500 gram, dissolved in ethyl acetate (14.95 c.c.) and examined in a 2-dm. tube at 16°, gave  $\alpha_D - 5.27^\circ$ , whence  $[\alpha]_D - 157.6^\circ$ , a number practically identical in magnitude with that given by the pure *d*-acid. Although there is no doubt that both the *d*- and *l*-acids

examined were practically pure, the very close agreement in the numbers is perhaps only fortuitous, inasmuch as the rotatory power is very sensitive to alteration of temperature. Comparative crystallographic examination of the *d*- and *l*-acids failed to reveal any difference whatever. When mixed in equal proportions, they fused at the melting point of the ordinary inactive acid.

The greater part of the expense incurred in this investigation was defrayed by a grant from the Research Fund of the Chemical Society, and for this the authors desire to acknowledge their indebtedness.

CHEMICAL DEPARTMENT,  
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### CXXXIX.—*The Bromination of Silver Cyanate.*

By GEORGE DEAN, M.A.

DURING some experiments on the preparation of certain cyanogen compounds, equivalent weights of silver cyanate and bromine were taken in a sealed tube and gently heated, the bromine being introduced in a thin glass bulb. On opening the tube, most of the halogen had disappeared, only a trace of vapour remaining in the enclosed air. The solid residue appeared to be an additive compound of silver cyanate and bromine. When heated, it gave off bromine, and on the addition of water decomposed with effervescence, bromine being evolved. Other specimens, which had been freed from uncombined bromine by being kept for several weeks over caustic soda, iron filings, or in a vacuum, behaved similarly.

The substance was of a brittle, friable nature, and had a deep yellow colour quite distinct from that of silver bromide; when exposed to light in a tightly-stoppered bottle, it preserved its colour indefinitely. In the presence of traces of moisture, silver bromide was produced, the colour fading to a pale yellow which slowly blackened. When a tube containing the substance was plunged into a bath of sulphur at 300—400°, the bromine evolved was accompanied by a thick white sublimate of cyanogen bromide. At that temperature, an interaction had evidently taken place between part of the liberated halogen and the silver cyanate.

The following experiment was made in order to find out the reacting proportions. Ten grams of cyanate were placed in a small, stoppered

distilling flask and bromine added until the whole was liquid. During the reaction, the heat evolved was sufficient to produce an appreciable rise in temperature. Next morning, the dark brown mass had solidified, and showed signs of crystalline structure, the surface being crossed by several fine long needles.

The greater portion of the excess of bromine present was drawn off with the aid of the water-pump, but some difficulty was experienced in getting rid of the last traces without having to raise the temperature. On gently heating, a few minute rosettes of needle-shaped crystals were seen to have condensed from the vapour. These crystals, which volatilised during the course of the experiment, probably consisted of cyanogen bromide.

The final weight of the brominated cyanate was 15.065 grams, corresponding with an addition of 76 units per molecule of the silver salt.

The presence of cyanogen bromide in the vapour would be explained if the reaction on bromination had followed the course represented by the equation :



In that case, it should have been accompanied by free oxygen. To determine if this were so, several grams of silver cyanate were treated with bromine in an exhausted flask and the gas pumped out by means of a Sprengel pump. About 80 c.c. were obtained and found on analysis to be a mixture of carbon dioxide and nitrogen, roughly in the proportions 1 to 2.5, but no oxygen was present. The bromine used had not in this instance been specially dried, and I suspected that the gas produced might be due to the oxidising action of the moist halogen, especially as the increase in weight after bromination was much lower than usual. The experiment was accordingly repeated with fresh material, which was prepared as follows. The silver cyanate was obtained by evaporating a solution containing silver nitrate and urea in molecular proportions. The mass of fine needle-shaped crystals which separated was repeatedly washed with hot water, drained, dried in a vacuum, heated for several hours at 100°, and finally left for some weeks over concentrated sulphuric acid in a vacuum. Commercial bromine was well washed with water, and then left with successive solutions of potassium bromide which removed chlorine and cyanogen chloride. Traces of iodine were eliminated by means of zinc oxide, and water was removed by fused zinc bromide. The bromine thus purified was finally distilled from fresh zinc bromide and the first and last portions of the distillate rejected.

On repeating the bromination in a vacuum with the dried substances, several grams of cyanate evolved only 5 c.c. of gas, consisting approximately of 1 vol. of carbon dioxide and 2 of nitrogen. In no instance

could any appreciable amount of oxygen have been produced, and the gas evolved is apparently due to a secondary reaction caused by the presence of water.

In order to determine the weight of bromine retained by the cyanate when the conditions of temperature and pressure were varied, the apparatus used was modified somewhat; bromination was effected in a Wurtz flask, provided with a well-ground stopper, the side-tube being connected with a large glass bulb, which also had two other outlets. One of these communicated with a water-pump, through a wash-bottle containing strong sulphuric acid, and the other could be quickly opened to the air. The glass bulb thus employed served as a trap between the flask and the drying bottle, and the latter prevented the passage of water vapour from the pump to the substance.

Much heat was evolved on bromination, and the product was then left until the next day, more bromine being added on successive days until the mass was quite liquid. Excess of bromine was then removed by heating the flask to about  $60^{\circ}$  in a water-bath and gradually diminishing the pressure to 300—400 mm. of mercury. As soon as the space above the solid appeared to be free from bromine vapour, the flask was disconnected and weighed. This gave the first determination of the added bromine. The flask was then replaced, exhausted, and weighed. The details of the separate treatments, together with the results obtained, are given below.

		Bromine.
1st exhaustion—	continued until no bromine vapour could be seen at $60^{\circ}$ under 300—400 mm. pressure. Increase in weight per molecule of cyanate.....	90.56
2nd	„ continued for 30 mins. at same temperature and pressure as before.....	82.6
3rd	„ continued for 30 mins. at same temperature and pressure as before.....	81.7
4th	„ continued for 30 mins. at same temperature and pressure as before.....	81.3
5th	„ continued for 30 mins. at same temperature and pressure as before.....	81.0
6th	„ after long exhaustion at $100^{\circ}$ (300—400 mm.)...	79.74
7th	„ after long exhaustion in the cold (300—400 mm.)	79.74
8th	„ after long exhaustion to 10—20 mm. in the cold	79.66
9th	„ on heating at $100^{\circ}$ for 15 mins., bromine was seen to be coming off, and therefore no weighing was made.	
10th	„ on heating at the temperature of a saturated calcium chloride solution, bromine was evolved.	

Bromine.

11th exhaustion—on heating at  $220^{\circ}$ , there was a steady evolution of bromine vapour, which was still being given off when the apparatus was disconnected 66.92

The conclusions drawn from the foregoing experiment are as follows :

1. The weight remains fairly steady when the composition of the product corresponds with the formula  $(\text{AgCNOBr})_x$ .

2. Dissociation does not take place below  $70^{\circ}$ , but begins below  $100^{\circ}$  and is not complete at  $200^{\circ}$ .

3. At the ordinary temperature, dissociation can be produced by lowering the pressure to 10—20 mm. of mercury.

#### *Action of Different Reagents on the Substance.*

*Water.*—Treatment with water causes an effervescence due to a mixture of gas and bromine vapour. In order to test the gas produced, the substance was introduced into a small flask provided with a dropping funnel and connected with a Sprengel pump by means of a tube packed with iron wire, to absorb the bromine. The flask was exhausted and the gas which was evolved on the addition of water was pumped out and tested; it proved to be a mixture of carbon dioxide and nitrogen in the proportions by volume of 2.5 of the former to 1 of the latter. The solid residue was chiefly silver bromide, but contained in addition a white constituent. To obtain a specimen of this, 10 grams of cyanate were brominated and the product treated with water after removing the excess of halogen. The dry residue weighed 13.6 grams instead of 12.53, as calculated for silver bromide. By careful levigation, a little of the white portion was removed from the bromide and tested. It answered the tests for cyanuric acid, and on combustion the percentages of carbon and hydrogen agreed fairly well with the calculated values. The action of water on the substance is approximately represented by the following equation :



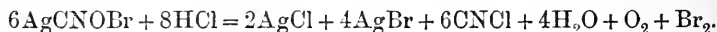
*Alcohol.*—Absolute alcohol was heated with some of the substance, when a slight evolution of gas took place and a distinct odour of aldehyde was observed. The liquid turned yellow and reduced ammoniacal silver solution. A white deposit settled on the surface of the silver bromide, but was not further examined. The reaction probably took the following course :



*Ammonia.*—When well-dried ammonia was passed over about 10 grams of the substance enclosed in a tube, white fumes were formed

and a considerable evolution of heat was noticed. The yellow residue, unlike the original substance, then rapidly turned dark, and on further heating gave, in addition to a little ammonium bromide, a white sublimate insoluble in water.

*Hydrogen Chloride.*—On passing the dried gas over the substance, bromine was at first given off, the amount increasing on gently heating. At the same time, a few drops of clear liquid distilled which gradually turned milky and finally solidified; this product was probably cyanogen chloride, the residue being a mixture of silver chloride and bromide:



### *A Higher Additive Compound.*

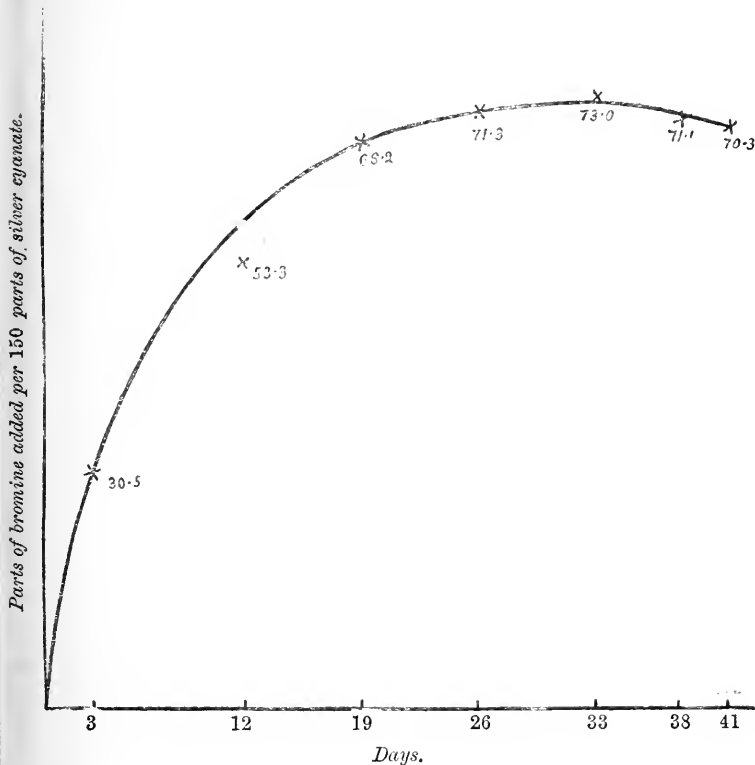
Evidence was not wanting of the existence of a more unstable product containing a larger proportion of bromine. In the second experiment, the dark brown solid product had the appearance of such a compound, and as the excess of bromine was removed it lost its superficial crystalline structure. This fact is supported by the following experiments, which were made in order to determine whether bromination at a lower temperature would have any effect on the reacting proportions.

To bring about interaction at a low temperature, bromine vapour was allowed to diffuse gradually in through the silver cyanate. The apparatus used consisted of a small retort, tightly stoppered, to the neck of which a flask was ground. Into the latter, the cyanate was introduced, whilst the bromine was poured into the retort. The progress of the reaction could be traced from the movement of the encroaching ring of additive compound in the mass of cyanate. From time to time, the apparatus was disconnected, the vapour in the flask removed by a current of air, and the increase in weight determined. The rate at which the halogen was taken up diminished gradually, and after about thirty days there was no further addition, the increase then corresponding with 73 parts per molecule of cyanate. After that, the proportion of bromine diminished, a slight decomposition taking place, due probably to the presence of moisture in the aspirated air. The following curve shows the rate of bromination.

Bromine and cyanate from the same samples as those used in the foregoing experiments were next allowed to interact in exactly the same manner, but for a longer period. No disturbance of the apparatus was made for intermediate weighing. On attempting to remove the free vapour from the flask before weighing, by passing air through as before, a copious and prolonged evolution of bromine took place. On weighing the added bromine at this stage, there were still 120 parts

per molecule of cyanate. On again passing air through the flask, more bromine was expelled, and the ordinary yellow product remained.

In order to see whether this additional absorption of bromine could be attributed to any purely mechanical action of the finely-divided compound, an experiment was performed, precisely similar in method, but in which the cyanate was replaced by dry precipitated barium sulphate. No absorption whatever took place, the sulphate remaining



absolutely constant in weight after several months' immersion in the vapour.

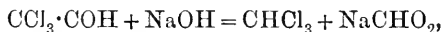
I have much pleasure in thanking the Research Committee of the Chemical Society for a grant, which has defrayed part of the cost of the materials used in the foregoing experiments.

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CXL.—*The Decomposition of Chloral Hydrate by Sodium Hydroxide and by Certain Salts.*

By EMIL ALPHONSE WERNER.

THE well-known decomposition of chloral by the caustic alkalis, which has been supposed to take place in accordance with the generally accepted equation :



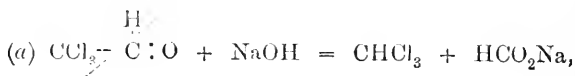
is frequently employed to illustrate :

(1) The ease with which chloroform can be generated from chloral.

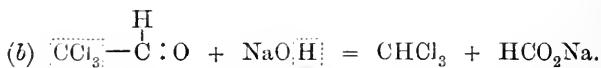
(2) A simple, rapid, and accurate method for the volumetric estimation of the amount of chloral in solution in the absence of substances which interfere with the reactions.

On considering this decomposition, perhaps the most interesting feature of the change is the very rapid and quantitative production of formic acid or a formate.

The foregoing equation does not appear to have ever been called in question, and, assuming for the present that it correctly represents the decomposition, it is obvious that the form of the equation may be expressed in two ways, thus :



or



It is not, however, easy to decide to which of these equations preference should be given, and the experimental evidence derived from the study of the decomposition of various chloral derivatives does not lend much aid.

In view of the results described in the present communication, it would be idle to discuss these various points, but if, for the sake of argument, equation (a) is to be assumed as being probably the more correct, one would have in this case a rapid and direct synthesis of a formate from "nascent" carbon monoxide\* and sodium hydroxide

\* Since the molecular formula of carbon monoxide is CO, it might be argued that a "nascent" state is not consistent with such a case. It is, however, quite possible that this oxide, as we know it in the free state, may be C≡O (that is, with quadri-valent oxygen), in which case its "nascent" state might be represented as >C=O, this modification being capable of uniting at the ordinary temperature with sodium hydroxide to yield sodium formate, or with water to form formic acid.

under conditions which are in marked contrast with the well-known behaviour of the monoxide towards the caustic alkalis.

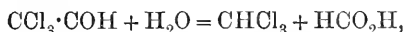
In the hope of throwing further light on the nature of this reaction, an investigation was commenced some time ago, and although it is, as yet, far from complete, some interesting and rather unexpected results have been obtained.

*Behaviour of Chloral Hydrate towards Dilute Acids and Water.*

Whilst chloral is instantly decomposed in contact with alkalis, even at the ordinary temperature, its stability towards dilute acids is, in view of the following facts, somewhat remarkable. When heated in a sealed tube at  $150^{\circ}$  with dilute sulphuric acid (1 : 7), chloral does not afford any chloroform or formic acid, and the solution gives only a faint opalescence with silver nitrate. Dilute acetic acid (1 : 10) at  $170^{\circ}$  is likewise without action on chloral.

When heated with water alone, chloral shows great stability. A 10 per cent. solution of the hydrate heated for two hours at  $190-200^{\circ}$  does not give even a trace of chloroform or formic acid, and the crystalline hydrate itself, after heating for four hours at  $250^{\circ}$ , gave a solution in water which was just faintly acid owing to hydrochloric acid, and contained 93.7 per cent. of unchanged chloral. A small quantity of carbonyl chloride is formed, but no chloroform or formic acid.

These facts seem to dispose of the idea, which has apparently been current, that the decomposition of chloral by an alkali is comparable to a hydrolytic decomposition, and may be simply expressed as

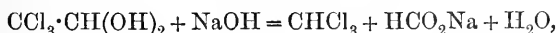


an equation which appears in some text-books.

*Decomposition of Chloral by Sodium Hydroxide.*

When the theoretical amount of normal sodium hydroxide solution is directly added to a dilute solution of chloral hydrate (10 or 12 per cent.), the decomposition proceeds immediately, but at the ordinary temperature is not complete until after the lapse of four or five hours.

If the liquid is titrated directly after mixing, it is found that from 7 to 8 per cent. of the chloral has remained undecomposed. If the solution is heated on the water-bath, the decomposition is completed in a few minutes, in accordance with the equation :



which has been generally accepted as representing the final action of the alkali.

This equation does not, however, represent the full decomposing power of the sodium hydroxide.

The results of the following experiments show that the quantity of chloral decomposed by one molecular proportion of sodium hydroxide is a function of the temperature, and that free formic acid can be readily generated.

In the following experiments, the chloral hydrate was heated with 10 c.c. of normal sodium hydroxide solution in a sealed tube to the required temperature until the decomposition was completed, and the formic acid generated was directly titrated.

*Expt. 1.*—Chloral hydrate (3.31 grams = 2 mols.), and sodium hydroxide (10 c.c. = 1 mol.), were heated at 120° for 1 hour. The total acidity of the product was equivalent to 10.7 c.c. of the alkali. The amount of formic acid produced according to the equation :



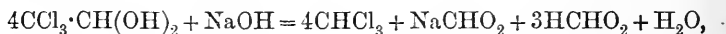
requires 10 c.c. of the alkali ; the slight excess of acidity is due to a small amount of chloroform decomposed with the production of a trace of hydrochloric acid ; this is found to occur in all the experiments ; the excess of acid over the theoretical amount, which, as might be expected, increases with the temperature, will be simply referred to as the "chloroform decomposition."

*Expt. 2.*—Chloral hydrate (4.96 grams = 3 mols.), and sodium hydroxide (10 c.c. = 1 mol.) were heated at 160° for 2 hours. The total acidity of the product was equivalent to 22.8 c.c. of the alkali. The theory for the equation :



indicates 20 c.c. of the alkali, the excess required being due to chloroform decomposition.

*Expt. 3.*—Chloral hydrate (6.62 grams = 4 mols.), and sodium hydroxide (10 c.c. = 1 mol.), were heated at 180° for 2 hours. The total acidity of product was equivalent to 40.8 c.c. of the alkali. The theory for equation :



requires only 30 c.c. of alkali. The large excess of acid equivalent to 10.8 c.c. of alkali is here again due to chloroform decomposition at the high temperature. A determination of chlorine precipitated by silver nitrate showed that 1.45 grams of chloroform had been decomposed.

It is quite evident from the foregoing experiments that sodium hydroxide can decompose one, two, three, or four molecular proportions of chloral hydrate according to the temperature maintained, and

in the last three cases we have the peculiar instance of a neutral substance, when decomposed by an alkali, giving a strongly acid liquid.

Whether the formic acid originates from the union of "nascent" CO and  $\text{H}_2\text{O}$  or from the union of  $-\text{COH}$  and  $-\text{OH}$  it is not easy to decide, although one is inclined from other considerations to favour the former view of the reaction.

### *Decomposition of Chloral Hydrate by Salts.*

It was obvious from the foregoing results that chloral hydrate could be decomposed by certain salts, such as sodium formate and its homologues. Experiments showed that whilst formate, acetate, propionate, butyrate, and valerate of sodium are without action on a solution of chloral in the cold, they all readily effect its decomposition on heating at  $120$ — $140^\circ$ . With the formate, for example, at  $120^\circ$ , the decomposition into chloroform and formic acid is complete. Sodium oxalate and succinate can also effect the decomposition of chloral hydrate at  $140^\circ$ , the succinate being the more effective.

Sodium acetate was selected as being the most convenient salt for studying some further points connected with this chloral decomposition.

At  $120^\circ$ , the acetate can effect the complete decomposition of a molecular proportion of chloral hydrate after 1 hour's heating.

At  $160^\circ$ , after 2 hours' heating, one molecular proportion of the acetate brought about the decomposition of two molecular proportions of the hydrate; thus, on using 3.31 grams of chloral hydrate and 1.36 grams of  $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$  dissolved in 10 c.c. of water, the total acidity is equivalent to 25.2 c.c. of sodium hydroxide; the theory for the foregoing proportions is 20 c.c., the excess required, namely, 5.2 c.c. of the alkali, being due to chloroform decomposition.

At a higher temperature, a still larger proportion of the chloral can be decomposed by the acetate, but the liquid becomes dark brown with the separation of tarry matter, and hence these experiments were not carried any further.

Seeing that dilute acids are not capable of decomposing chloral hydrate, experiments were next made with the object of ascertaining to what extent the presence of free acid at the outset is capable of interfering with the decomposing action of a salt such as sodium acetate.

The results of the following experiments prove that even in the presence of a large excess of acetic acid, sodium acetate is still capable of effecting the complete decomposition of the chloral hydrate, even without any appreciable alteration in the temperature.

*Expt. 4.*—Chloral hydrate (3.31 grams = 1 mol.), 2.72 grams of  $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$  (1 mol.), 1.2 grams of  $\text{C}_2\text{H}_4\text{O}_2$  (1 mol. = 20 c.c. NaOH), and 10 c.c. of  $\text{H}_2\text{O}$  were warmed under pressure. Chloroform

gradually separates at  $100^{\circ}$ ; on heating at  $130$ — $140^{\circ}$  for 1 hour, the decomposition is complete. The total acidity of the product is equivalent to 44.9 c.c. of sodium hydroxide, whilst the theoretical value for complete decomposition is 40 c.c. The excess of alkali required is due to chloroform decomposition.

*Expt. 5.*—Similar to the preceding experiment, but with 2.4 grams of acetic acid (2 mol. proportions = 40 c.c. NaOH). No visible decomposition at  $100^{\circ}$  even after 2 hours, but the reaction was complete after 1 hour at  $150^{\circ}$ . The total acidity of product was equivalent to 65.2 c.c. of the alkali, whereas the theoretical value for complete decomposition is 60 c.c. The excess of alkali was due to chloroform decomposition; on opening the tubes, some carbon monoxide was detected by palladium chloride paper.

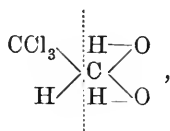
*Expt. 6.*—As in the foregoing experiments, but with 4.8 grams of acetic acid (4 mol. proportions = 80 c.c. NaOH), the mixture being heated for 2 hours at  $170^{\circ}$ . The total acidity of product was equivalent to 104 c.c. of alkali, the calculated value for complete decomposition being equal to 100 c.c. The small excess was again due to chloroform decomposition, although a small quantity of the chloral hydrate (0.42 gram) was still undecomposed.

Thus the chloral hydrate is decomposed by the acetate into chloroform and formic acid, whether a large excess of free acetic acid is present or not. In reality, the formic acid displaces acetic acid from the acetate; this is proved by distilling the product from the decomposition, when no formic acid is found in the distillate.

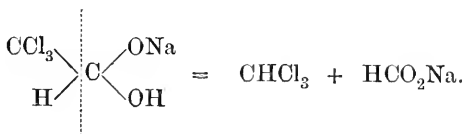
Before discussing the results of these experiments, I may mention that the salts of the mineral acids, such as sodium chloride, sulphate, and phosphate, are also capable of effecting the complete decomposition of chloral hydrate at a temperature of  $120$ — $170^{\circ}$ , whilst such salts as copper sulphate and ferrous sulphate do not bring about a decomposition at these temperatures.

The outcome of this investigation goes to prove that the usually adopted equation given at the commencement of this paper is substantially incorrect and has really no foundation in fact.

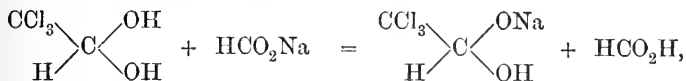
In order to discuss the decomposition of chloral by sodium hydroxide or sodium acetate, it is absolutely necessary to take into consideration the structural formula of chloral hydrate itself, when the decomposition then appears to be brought about in the manner indicated by the following diagram:



the hydrate decomposing directly into chloroform and formic acid when in contact with the alkali or salts. The decomposition of a relatively large proportion of the hydrate at the higher temperature is easily explained on the assumption that a sodium derivative is first produced, which immediately decomposes, thus :



On raising the temperature, the formate probably interacts with chloral hydrate in the following manner :



the sodium derivative again decomposing, so that chloroform, sodium formate, and formic acid now form the products, these changes being repeated up to a certain limit, depending on the temperature.

The fact that the diacetyl derivative,  $\text{CCl}_3 \cdot \text{CH}(\text{OAc})_2$ , is not decomposed by cold sodium hydroxide (Geuther, *Annalen*, 1858, 106, 249), whilst trichloroacetal,  $\text{CCl}_3 \cdot \text{CH}(\text{OEt})_2$ , is not affected even by a boiling solution of the alkali, is in complete accordance with the above view of the nature of the decomposition. If this explanation is correct, it would seem to dispose at once of the idea of the possible existence of a "nascent" carbon monoxide put forward in the earlier part of this paper in order to explain the decomposition. Further experimental evidence is, however, necessary before completely discarding this view.

Attempts to decompose chloral hydrate alone directly into chloroform and formic acid were not successful.

When the hydrate is heated alone in a sealed tube, the liquid separates into two layers at  $190^\circ$ ; on cooling, all the hydrate is regenerated. If the temperature is raised to  $250^\circ$ , only 8.65 per cent. of the hydrate is decomposed, even after four hours' heating; some hydrochloric acid (resulting from the action of water on carbonyl chloride) is produced, but neither chloroform, formic acid, nor even carbon monoxide is found to be present.

A ten per cent. aqueous solution of the hydrate, after heating for two hours at  $190^\circ$ , likewise failed to give even a trace of chloroform or formic acid.

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CXLI.—*Contributions to the History of Glyoxylic Acid.*

By HEINRICH DEBUS, Ph.D., F.R.S.

I DISCOVERED glyoxylic acid (Debus, *Phil. Mag.*, 1856, 12, 361, and 1857, 13, 39, 66) in 1856 as one of the products of the oxidation of ethyl alcohol by nitric acid at common temperatures, and in 1886 it was detected by H. Brunner and E. Chuard (*Ber.*, 1886, 19, 595, 616; 1891, 24, 3305) as one of the constituents of the juice of unripe grapes, apples, plums, gooseberries, currants, and rhubarb; v. Lippmann also found it a few years later in the young roots of the beet plant.

As the fruit ripens, the acid diminishes in quantity and sugar appears to be formed. These chemical changes can perhaps be explained by the observations of Fenton (*Trans.*, 1900, 77, 70, 1296), Hopkins and Cole (*Proc. Roy. Soc.*, 1900, 68, 27), and Ollendorf. According to these chemists, glyoxylic acid and formaldehyde are produced by the oxidation of acetic or glycollic acid by hydrogen peroxide in presence of ferrous sulphate. Fenton has pointed out that glyoxylic acid,  $\text{COH}\cdot\text{CO}_2\text{H}$ , appears to be an intermediate product between glycollic acid,  $\text{CH}_2(\text{OH})\cdot\text{CO}_2\text{H}$ , and formaldehyde,  $\text{HCOH}$ .

By catalytic action, glyoxylic acid could decompose into carbon dioxide and formaldehyde, and the latter, by a process of condensation, could form carbohydrates of higher molecular weight, such as belong to the class of sugars. In this way, the disappearance of the acid and the formation of sugar could be explained.

Crystallised glyoxylic acid,  $\text{C}_2\text{H}_4\text{O}_4$ , is polymeric with formic acid, and esters of both acids are produced from hydrogen cyanide, hydrogen chloride, and ethyl alcohol under conditions in which only esters of formic acid might be expected (Pinner and Klein, *Ber.*, 1878, 11, 1480).

Formic acid again appears to be the only direct product of the reduction of carbon dioxide by nascent hydrogen at common temperatures, irrespective of the mode by which the nascent hydrogen is produced (Coehn and Jahn, *Ber.*, 1904, 37, 2836). These considerations render glyoxylic acid especially interesting from a physiological point of view. In consequence, it has repeatedly been investigated by chemists, amongst others by Beckurts and Otto (*Ber.*, 1881, 14, 576, 1616), and by Doebner and Glass (*Annalen*, 1900, 311, 129; 1901, 317, 147). Some of the experimental results of these investigators, however, do not agree with older observations of my own, and as it is my wish to render my own work as accurate as possible, I have in

the Davy-Faraday Laboratory of the Royal Institution, London, repeated such of my experiments as are not in accord with the observations of the above-named investigators.

*The Formula of Glyoxylic Acid.*

Besides glyoxylic acid, I discovered amongst the products of the oxidation of ethyl alcohol by nitric acid a new aldehyde, namely, glyoxal. As both these substances were at first obtained in the form of syrupy liquids, their composition was deduced from the analysis of some well characterised salts. In this way, the formula  $C_2H_4O_4$  was found for the acid. It was shown that glyoxylic acid, like glyoxal, possessed the characteristic properties of the aldehydes. Both produce on glass a mirror of metallic silver when warmed with an ammoniacal solution of silver nitrate, both combine with sodium hydrogen sulphite and exchange oxygen for sulphur when treated with hydrogen sulphide. The direct analysis of pure glyoxal led to the formula  $C_2H_2O_2$ . Heated with dilute nitric acid on a water-bath, it is oxidised to glyoxylic and oxalic acids.

As the acids produced from aldehydes by direct combination with oxygen contain the same number of hydrogen atoms as the latter substances, it follows that glyoxylic acid ought not to contain more hydrogen atoms in one molecule than glyoxal or oxalic acid. The formula  $C_2H_4O_4$ , previously adopted for glyoxylic acid, was accordingly changed to  $C_2H_2O_3 \cdot H_2O$ . The molecule of water of this formula cannot be removed by heating the acid at  $100^\circ$  or a higher temperature without causing a more extensive decomposition. The anhydrous acid,  $C_2H_2O_3$ , has not yet been obtained. Also all the salts, with the exception of the ammonium salt,  $C_2H(NH_4)O_3$ , contain water. In consequence, some chemists retain for glyoxylic acid the original formula  $C_2H_4O_4$ , whilst others have adopted the formula  $C_2H_2O_3$ . Perhaps there are two acids,  $C_2H_2O_3$  and  $C_2H_4O_4$ , easily convertible into each other by reversible processes similar to pyro- and ortho-phosphoric acids. But I consider that the formula  $C_2H_2O_3$  is sufficient for the explanation of all facts. I will, in order to facilitate a correct judgment, describe in the following lines the reasons which may be advanced in favour of each formula.

The formula  $C_2H_2O_3$  is principally supported by the following considerations:

(1) The oxidation of ethyl alcohol at common temperatures takes place in two stages (Debus, *Journ. Chem. Soc.*, 1866, 19, 17). In the first stage two atoms of hydrogen are withdrawn from one molecule of alcohol, and in the second stage one atom of oxygen is put into the place of the hydrogen atoms thus removed. This process is repeated

until the molecule is charged with as many oxygen atoms as it can hold without decomposition. In this way we obtain:

Alcohol, $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{OH}$ .	Glycollic acid, $\text{CH}_2(\text{OH}) \cdot \text{CO}_2\text{H}$ .
Acetaldehyde, $\text{CH}_3 \cdot \text{COH}$ .	Glyoxylic acid, $\text{COH} \cdot \text{CO}_2\text{H}$ .
Acetic acid, $\text{CH}_3 \cdot \text{CO}_2\text{H}$ .	Oxalic acid, $\text{CO}_2\text{H} \cdot \text{CO}_2\text{H}$ .

The successive formation of these derivatives is one of the best proofs that ethane contains two methyl groups. Both groups may undergo the same change simultaneously:

Ethane .....	$\text{CH}_3 \cdot \text{CH}_3$ .
Glycol.....	$\text{CH}_2(\text{OH}) \cdot \text{CH}_2 \cdot \text{OH}$ .
Glyoxal .....	$\text{COH} \cdot \text{COH}$ .
Oxalic acid .....	$\text{CO}_2\text{H} \cdot \text{CO}_2\text{H}$ .

The oxidation of all alcohols and their derivatives appears to take place according to these rules.

From the analogous changes of the two methyl groups in ethane, we may conclude that glycollic, glyoxylic, and oxalic acids stand in the same relation to each other as do alcohol, aldehyde, and acetic acid. In other words, if the formulæ of glycollic and oxalic acids respectively are  $\text{CH}_2(\text{OH}) \cdot \text{CO}_2\text{H}$  and  $\text{CO}_2\text{H} \cdot \text{CO}_2\text{H}$ , then the intermediate glyoxylic acid will probably be  $\text{COH} \cdot \text{CO}_2\text{H}$ , and will, when crystallised, contain one molecule of water of crystallisation.

(2) This conclusion is supported by the chemical properties of formaldehyde and other aldehydes.

According to Loew, the action between bases and formaldehyde (*Jahresber.*, 1888, 1515—1516) always produces methyl alcohol and formic acid. Tollens also found that a mixture of formaldehyde, water, and magnesia at  $130^\circ$  produces methyl alcohol and formic acid.

Acetaldehyde reacts apparently in a similar manner. Heated with potassium hydroxide in an aqueous solution, it produces a dark, resinous substance and potassium acetate. If the reaction were analogous to the one with formaldehyde, ethyl alcohol ought to be produced.

But ethyl alcohol is easily converted by caustic alkalis into a brown, resinous substance, and this reaction does really seem to occur when potassium hydroxide acts on acetaldehyde. Berzelius says: "The brown resin appears to be in a continuous state of change, and at the same time it gives out a spirituous odour" (Berzelius, *Lehrbuch*, 3rd edition, 8, 330).

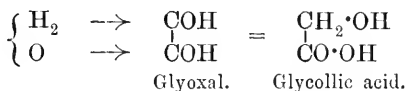
According to this description, it appears probable that the ethyl alcohol, which should be produced by a mixture of potassium hydroxide, water, and acetaldehyde, is, while in the nascent state, at once converted into the brown resin.

Valeraldehyde reacts with alkalis, like formaldehyde, yielding amyl alcohol and valeric acid.

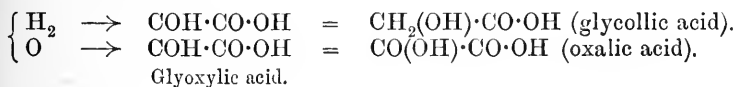
*n*-Heptaldehyde, placed for a few weeks in contact with pieces of quicklime, loses the elements of water and becomes converted into hydrocarbons. The elements of water, in their turn, react with other portions of *n*-heptaldehyde and produce *n*-heptyl alcohol and *n*-heptoic acid. Oil of bitter almonds reacts with potassium hydroxide in the same way.

The reaction appears to be a characteristic one for aldehydes, and to be due to the presence of the group COH.

If this conclusion is correct, then glyoxal, which contains the group COH twice, ought with lime-water to produce calcium glycollate :



the alcoholic and the acid properties remaining united in one molecule. Numerous experiments have confirmed this conclusion. And glyoxylic acid, which contains the group COH only once, ought to produce with alkalis calcium glycollate and oxalate. Also this deduction agrees with the experimental results.



This reaction is quantitatively exact when calcium glyoxylate is boiled with lime-water. From the facts described in the foregoing lines, I conclude that glyoxylic acid contains the group COH, and that the formula of the crystallised acid is COH·CO·OH, H<sub>2</sub>O.

(3) Glyoxylic acid will dissolve zinc without evolution of hydrogen and form basic zinc glycollate, Zn(OH)·C<sub>2</sub>H<sub>3</sub>O<sub>3</sub>. Glyoxylic acid acts like an unsaturated compound.

(4) Glyoxylates and acid sulphites form well-defined compounds (*Annalen*, 1863, 126, 130; *Phil. Trans.*, 1863, 153, 437), of which the sodium derivative, CH(OH)(SO<sub>2</sub>·ONa)·CO<sub>2</sub>Na, is an example.

(5) Glyoxylates exchange oxygen for sulphur when treated with hydrogen sulphide (*Phil. Trans.*, 1863, 153, 447), thus the calcium salt yields the compound Ca(C<sub>2</sub>HO<sub>3</sub>)·C<sub>2</sub>HO<sub>2</sub>S, 3H<sub>2</sub>O.

(6) Glyoxylates exhibit a strong affinity for ammonia (*Phil. Trans.*, *ibid.*).

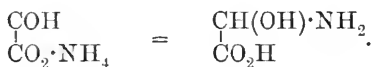
(7) Hydroxylamine and phenylhydrazine react with glyoxylic acid as they do with aldehydes (*Jahresber.*, 1892, 1382; *Ber.*, 1884, 17, 577), forming oximidoacetic acid, CH(:NOH)·CO<sub>2</sub>H, and the corresponding hydrazone, C<sub>6</sub>H<sub>5</sub>·NH·N:CH·CO<sub>2</sub>H.

(8) All these reactions point to the presence of the group COH in glyoxylic acid, or, in other words, glyoxylic acid acts as if it did contain this group. In agreement with this behaviour is the composition of the ammonium salt (*Annalen*, 1859, 110, 327), which was prepared by the double decomposition of calcium glyoxylate and ammonium oxalate and evaporation of the solution over sulphuric acid in a vacuum.

For this purpose, it is not necessary to dissolve the calcium glyoxylate completely in water. It is sufficient to mix intimately equivalent quantities of the salts, and add about as much water to the mixture as is necessary to dissolve the resulting ammonium glyoxylate, and leave the mixture to digest until the liquid no longer reacts with calcium salts for oxalates or with oxalates for calcium.

The filtered liquid is then concentrated over sulphuric acid under diminished pressure. The evaporation must not be performed on a water-bath on account of the facility with which the salt decomposes.

Ammonium glyoxylate crystallises very well and is easily soluble in water, forming a neutral solution, which becomes acid on evaporation over sulphuric acid. W. H. Perkin, sen., has suggested that this change in the reaction with blue litmus paper might be due to a change in the arrangement of the atoms of the salt, and that the ammonia salt probably changed during the evaporation according to the equation :



My experiments do not support this view. The ammonium glyoxylate is, according to my observations, a salt like ammonium oxalate. With a cold and not very strong solution of potassium hydroxide it will at once produce volumes of ammonia, with platinic chloride it yields ammonium platinichloride, and on the addition of calcium nitrate the formation of a precipitate of calcium glyoxylate takes place. This precipitate appears at first in the form of a dense jelly, which in the course of a few hours turns into crystals like the original ammonium glyoxylate.

The change of reaction with blue litmus paper from neutral to acid is not peculiar to ammonium glyoxylate. Most salts of ammonia are known to dissociate under similar conditions in the same way. Therefore, we cannot conclude that the acidification of ammonium glyoxylate solution, during the evaporation over sulphuric acid under diminished pressure, is due to a molecular change from an ammonium salt to an amide.

The facts described in this and former papers leave no doubt that there is a salt corresponding with the formula  $\text{COH} \cdot \text{CO}_2 \cdot \text{NH}_4$ .

The metallic salts of glyoxylic acid contain at least one molecule of water more, and are represented by the general formula  $\text{COH} \cdot \text{CO}_2\text{M}', \text{H}_2\text{O}$ . But as the aqueous solutions of these salts exhibit the chemical properties of compounds of the group  $\text{COH}$ , we must allow that the solutions of the metallic salts of glyoxylic acid are really solutions of salts of the acid  $\text{COH} \cdot \text{CO}_2\text{H}$ , and contain as solids, like the acid itself, water of crystallisation.

The presence of at least one molecule of water in these metallic salts is the principal reason why some chemists adopt for glyoxylic acid the formula  $\text{CH}(\text{OH})_2 \cdot \text{CO}_2\text{H}$ , and not the one here recommended, namely,  $\text{COH} \cdot \text{CO}_2\text{H}, \text{H}_2\text{O}$ .

Glyoxylates decompose at higher temperatures with great facility. Even calcium glyoxylate, one of the most stable, is partially decomposed to the extent of about half per cent. in boiling aqueous solutions. It is natural that salts of such a changeable nature cannot be rendered anhydrous without decomposition. In recent times, Doebner and Glass (*Annalen*, 1901, 317, 147) have described salts of potassium, sodium, calcium, strontium, barium, magnesium, aluminium, nickel, and cobalt as anhydrous glyoxylates, that is, as salts of the acid  $\text{C}_2\text{H}_2\text{O}_3$ . It is to be regretted that they have forgotten to prove that their salts were really undecomposed glyoxylates. Their results could also be explained in another way, which will be considered further on.

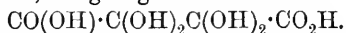
In favour of the formula  $\text{C}_2\text{H}_4\text{O}_4$  for glyoxylic acid, the following facts have been advanced.

(1) A mixture of crystallised glyoxylic acid and ethyl alcohol heated at  $120^\circ$  produces, according to W. H. Perkin, sen., the ester  $\text{C}_2\text{HO}(\text{C}_2\text{H}_5\text{O})_3 = \text{CH}(\text{C}_2\text{H}_5\text{O})_2 \cdot \text{CO}(\text{C}_2\text{H}_5\text{O})$ . According to Beilstein (*Handbuch*, 3rd edition, vol. i, p. 630), "the alkyl derivatives of glyoxylic acid place the formula  $\text{C}_2\text{H}_4\text{O}_4$  beyond doubt." In other words, if we replace the groups  $\text{C}_2\text{H}_5\text{O}$  by hydroxyl, the result will be glyoxylic acid,  $\text{CH}(\text{OH})_2 \cdot \text{CO} \cdot \text{OH}$ .

Analogy does not support this opinion. Ethyl orthoformate and ethyl orthocarbonate, respectively, do not prove the formula  $\text{CH}(\text{OH})_3$  for formic, and  $\text{C}(\text{OH})_4$  for carbonic acid. Therefore, the opinion just quoted is not beyond doubt.

(2) There was a time when the opinion prevailed that only one equivalent of hydroxyl could be in combination with one and the same atom of carbon. This view rested principally on Simpson's unsuccessful attempts to prepare a glycol with only one atom of carbon or a glycerol with only two atoms of carbon in one molecule. Also no native substance was known with more hydroxyl equivalents than carbon atoms. This view has been changed principally through the investigation of carboxytartronic acid by Kekulé. He found that this

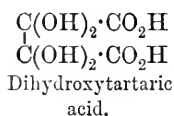
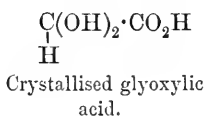
acid was also a product of the oxidation of tartaric acid, and called it dihydroxytartaric acid, assigning to it the formula



Since then, two equivalents of hydroxyl have frequently been assumed to be in combination with one atom of carbon.

Glyoxylic acid and dihydroxytartaric acid are related in several ways. When I examined calcium glyoxylate for the first time, I mistook it for calcium tartrate. Both salts are only sparingly soluble in water, both smell like burning sugar on a piece of red-hot platinum foil, and both produce a mirror of metallic silver with an ammoniacal silver nitrate.

Glyoxylic acid, with zinc in an acetic acid solution, will, like dihydroxytartaric acid, be converted into racemic acid (*Annalen*, 1883, 221, 259; *ibid.*, 1873, 166, 126; *Ber.*, 1892, 25, Ref. 462). Therefore, both acids probably contain the same or closely allied groups of atoms. If, in dihydroxytartaric acid, carbon atoms are present with two equivalents of hydroxyl attached to each, then it is very probable that the same mode of combination will also occur in the molecule of glyoxylic acid.

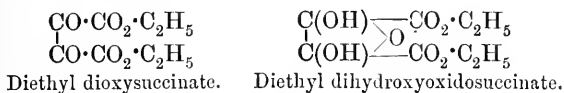


But is the constitution assigned to dihydroxytartaric acid sufficiently supported by facts? The answer to this question is not satisfactory. All salts of dihydroxytartaric acid contain water of crystallisation. Both acid and salts decompose very easily, a circumstance which renders the preparation of anhydrous dihydroxytartrates impossible. The acid melts and decomposes at 98° (Lash Miller, *Ber.*, 1889, 22, 2016). Fenton says: "Mere washing with water at ordinary temperature, for example, would cause a certain amount of decomposition into tartronate and carbon dioxide."

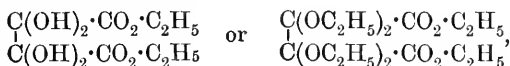
It is clear that such salts, when they contain water of crystallisation, cannot be deprived of the latter by the ordinary method. The ammonium salt appears even to be in a slow, continuous state of spontaneous decomposition at the ordinary temperature (*Trans.*, 1898, 73, 472). Kekulé heated the sodium salt in a dry current of air at 85° and kept it at this temperature for 540 hours. Only after this long-continued heating did the weight become constant. The original salt had the composition  $\text{C}_4\text{H}_4\text{Na}_2\text{O}_8, 2\frac{1}{2}\text{H}_2\text{O}$ . The escape of the water of crystallisation ought to have occasioned a loss of 16.6 per cent. in weight, whilst the actual loss was 27.6 per cent. Fenton, who examined the salts of potassium, sodium, ammonium, lithium,

rubidium, and caesium, found water of crystallisation in all, and he does not mention one case in which this water could be removed without decomposition of the salt.

Anschütz and Parlato produced two esters (Richter-Anschütz, *Organische Chemie*, 9th edition, I, 595), one, a green liquid, formed by acting on the sodium salt with a mixture of hydrogen chloride and alcohol, the other, a colourless, crystalline substance obtained by adding water to the former. The composition of these esters may be expressed by the formulæ:

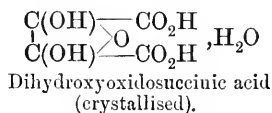


The ester of dihydroxytartaric acid,



was not obtained.

Therefore, the statement that the acid having the empirical formula,  $\text{C}_4\text{H}_6\text{O}_8$ , is dihydroxytartaric acid can only be taken as a hypothesis. The crystallised acid is probably represented by the following formula:



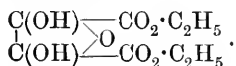
According to Kekulé's nomenclature, it would be called "dioxyoxosuccinic acid."

In accordance with this view, tartaric, dihydroxymaleic, and dihydroxyoxidosuccinic acids stand in the same relation as ethyl alcohol, acetaldehyde, and acetic acid. With this view of their constitution, the chemical behaviour of these substances is in harmony.

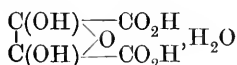
The composition of the esters prepared from dihydroxytartaric acid agrees with the foregoing formula. Anschütz and Parlato obtained by the action of hydrogen chloride on the sodium salt of dihydroxytartaric acid and alcohol:

Diethyl dioxysuccinate,  $\text{CO}_2(\text{C}_2\text{H}_5) \cdot \text{CO} \cdot \text{CO} \cdot \text{CO}_2 \cdot \text{C}_2\text{H}_5$ .

Diethyl dihydroxyoxidosuccinate,



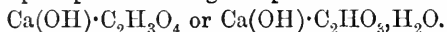
The existence of the latter compound supports the formula



for dihydroxytartaric acid.

From the above, it is clear that the reactions of Kekulé's dihydroxytartaric acid can be explained in a more simple manner by the view that it is dihydroxyoxidosuccinic acid with one molecule of water of crystallisation. But if it cannot be proved that in dihydroxytartaric acid two equivalents of hydroxyl are united to one atom of carbon, then one of the chief arguments in favour of this mode of combination in glyoxylic acid disappears.

There are some basic glyoxylates which can be considered as salts of the acid  $C_2H_4O_4$ . Lime-water produces with calcium glyoxylate solution a white precipitate having the probable formula



Similar salts of lead, copper, and manganese are known and will be described further on.

If all the foregoing statements be considered, it will be observed that only one salt, the ammonium compound,  $C_2HO_3(NH_4)$  (*Proc. Roy. Soc.*, 1859, 9, 711; *Annalen*, 1859, 110, 327), is known without water of crystallisation, and that the other salts of glyoxylic acid, in the solid state, contain at least one more molecule of water. But the solutions of these salts act with reagents like salts of the acid  $C_2H_2O_3$ .

Chemists who, on the strength of the empirical composition of the solid metallic salts, adopt for glyoxylic acid the formula  $C_2H_4O_4$ , must admit a second acid,  $C_2H_2O_3$ , and assume that the two acids,  $C_2H_2O_3$  and  $C_2H_4O_4$ , could, the first by combining with a molecule of water, the second by parting with a molecule of water, be transformed easily, forward and backward, one into the other. As, however, the reactions of the metallic salts of glyoxylic acid in aqueous solutions do not support this view, I will retain for glyoxylic acid the formula  $C_2H_2O_3$  as a sufficient expression for the explanation of all known facts.

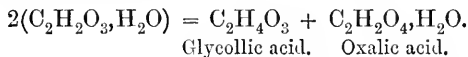
The following statements are supplementary to former communications of mine.

#### *Glyoxylic Acid.\**

An aqueous solution of glyoxylic acid evaporated under diminished pressure over concentrated sulphuric acid leaves a residue of syrupy consistency which will sometimes solidify to a crystalline mass of slightly yellow colour if allowed to remain for a longer time over the drying agent. The composition of this residue is expressed by the formula  $C_2H_2O_3, H_2O$ . The solid acid heated in a tube melts easily, and on reaching a certain temperature boils like water in similar circumstances. The bubbles of gas escaping from the liquid acid appear to be steam, which condenses on the sides of the tube, and

\* *Phil. Mag.*, 1856, 12, 361; *Annalen*, 1856, 100, 11.

the water runs back again into the liquid. If the heating is carefully continued until the boiling nearly ceases and the tube then allowed to cool down to the temperature of the air, the liquid acid will assume the appearance of jelly or glue. No distillate is formed, only a few c.c. of carbon dioxide escape during the heating. The residue in the tube is still soluble in water. But the aqueous solution now contains three acids, glyoxylic, oxalic, and glycollic acids. Hence, the effect of the heating has been a decomposition of a portion of the glyoxylic acid according to the following equation :



If the slightly brown residue in the tube is raised to a higher temperature than in the last experiment, it evolves carbon dioxide freely, and becomes more glutinous and dark brown in appearance without yielding a distillate. When allowed at this stage to become cold and treated with water and alcohol respectively, the brown, viscous residue is found to be almost insoluble in these reagents.

If the composition of one molecule of carbon dioxide is deducted from the composition of one molecule of glyoxylic acid, the elements of one molecule of formaldehyde and one molecule of water are left. The brown, glutinous residue must have formed from these elements at the high temperature at which the chemical change occurred, probably by a condensation of the elements of the aldehyde.

Crystallised glyoxylic acid is soluble in concentrated sulphuric acid ; the solution develops carbon monoxide without changing its colour when it is heated to 50—100°.

Mercuric oxide, prepared by the calcination of mercuric nitrate, is not reduced on warming in a solution of glyoxylic acid. Also cupric acetate and mercuric chloride respectively are not reduced under similar conditions. But potassium dichromate and potassium permanganate both yield a portion of their oxygen to a hot solution of glyoxylic acid.

Lead oxide heated in a solution of glyoxylic acid forms a white salt, but it does not turn the liquid alkaline, as would be the case with a solution of formic acid.

#### *Calcium Glyoxylate.\**

This salt, like calcium acetate, exists in two forms, one stable and crystallised, the other gelatinous and unstable. If a concentrated solution of ammonium glyoxylate is mixed with one of calcium nitrate, the mixture turns into a jelly, so that the vessel may be inverted without any loss. In the course of a few hours, white particles become

\* Debus, *loc. cit.*

visible in the mass; these particles increase gradually in number and magnitude, and develop finally into fine crystals having the form of the original calcium glyoxylate.

The crystals dissolve at  $8^{\circ}$  in 177 parts of water, and at  $100^{\circ}$  in about 40 parts. The hot saturated solution remains supersaturated for some time when allowed to cool down to the ordinary temperature, the excess of the dissolved salt crystallising out very slowly. Tufts of fine needles appear at first on the sides of the beaker, and as they grow larger they change in the course of a day or two into single prisms. The crystals thus obtained are very hard. The formula of the crystalline salt is  $\text{Ca}(\text{C}_2\text{HO}_3)_2 \cdot 2\text{H}_2\text{O}$ . When a solution of pure calcium glyoxylate is concentrated on the water-bath, the salt will, as the water evaporates, separate as a crust round the sides of the dish; if, however, calcium glycollate is present, the solution may be concentrated to a considerable extent without the separation of any salt.

The recrystallised calcium glyoxylate is never quite pure; if redissolved in water there always remains a small insoluble residue amounting to about half a per cent. This residue is insoluble in acetic, but soluble in hydrochloric acid. On a hot piece of platinum foil, it burns like calcium oxalate. As glyoxylates decompose easily into oxalates and glycollates, the appearance of calcium oxalate in a boiling solution of calcium glyoxylate is not difficult of explanation.

A weak solution of calcium glyoxylate can be boiled for some time without change. The solid salt contains one molecule of water of crystallisation, which, according to my experiments, cannot be removed at  $120^{\circ}$  in about five hours. At higher temperatures, decomposition of the salt takes place.

0.473 gram, dried over sulphuric acid, lost in four hours at  $115^{\circ}$  only 0.0015 gram in weight. Heated again, this time to  $120^{\circ}$  for three hours, it did not exhibit any further loss. Several experiments gave the same results.

Different results were obtained by Beckurts and Otto (*Ber.*, 1881, 14, 576, 1616), who found that crystallised calcium glyoxylate lost at  $140^{\circ}$  16.4 per cent. of its weight, and they attributed this loss to the escape of water. The residue left gave 17.7 per cent. of calcium. These numbers agree very well with the supposition that two molecules of water had evaporated;  $\text{Ca}(\text{C}_2\text{HO}_3)_2 \cdot 2\text{H}_2\text{O}$  requires  $\text{H}_2\text{O} = 16.2$  and  $\text{Ca} = 18.0$  per cent. Beckurts and Otto consider the residue left by the heated salt to be anhydrous calcium glyoxylate,  $\text{Ca}(\text{C}_2\text{HO}_3)_2$ . However, they also make a statement which is directly opposed to the results of their foregoing experiments, as will be seen by the following quotations (*loc. cit.*, 584): "the water of crystallisation of the calcium glyoxylate can be expelled without decomposition of the salt"; and on p. 1616 (*loc. cit.*) we read: "Only the ammonium salt

of glyoxylic acid crystallises in the anhydrous form, whilst all other salts of this acid contain water which cannot be removed without decomposition. . . ."

Twenty years later, Doebner and Glass determined the amount of metal and the water of crystallisation in various glyoxylates (*Annalen*, 1901, 317, 147). Their crystallised calcium glyoxylate lost at 110° 16·37 per cent. of water, and gave 17·99 per cent. of calcium. These numbers, although agreeing very well with those of Beckurts and Otto :

	Beckurts-Otto.	Doebner-Glass.
Water.....	16·40	16·37
Calcium .....	17·7	17·99

did not accord with my results : water, 0 ; calcium, 18·0 ; that is to say, that my crystallised calcium glyoxylate did not lose weight at 120°, whilst the salt of Doebner and Glass underwent a loss of 16·37 per cent. at 110°.

From this it seems clear that the salt obtained by Doebner and Glass and my calcium glyoxylate do not agree in properties, and therefore must be isomeric compounds.

Doebner and Glass also state that the crystals of their calcium glyoxylate are soft, whilst I found that those of my salt were very hard. They do not describe any other characteristic properties or reactions. These differences must be due to the distinct methods by which the glyoxylic acid was prepared.

Doebner and Glass prepared their glyoxylic acid from the decomposition products of dichloroacetates, whilst I extracted my acid from the mixture of substances resulting from the oxidation of ethyl alcohol at the ordinary temperature.

W. H. Perkin, sen., and Duppa discovered the formation of glyoxylic acid from silver dibromoacetate and water. I compared the calcium salt of the acid, thus prepared, with my calcium glyoxylate, and found them to be identical.

Doebner substituted for silver dibromoacetate potassium dichloroacetate and potassium acetate (*Annalen*, 1900, 311, 129).

The potassium glyoxylate produced was converted into the barium salt, and the latter decomposed by diluted sulphuric acid. The solution of the glyoxylic acid, after concentration at 20° in a vacuum, left a syrupy, colourless liquid, which, even at the temperature of a freezing mixture, could not be made to crystallise.

The combustion of the acid gave : C = 25·95, H = 4·83 ;  $C_2H_2O_3, H_2O$  requires C = 26·08, H = 4·34 per cent.

The hydrogen has been found to be 0·49 per cent. too high, this quantity exceeding considerably the errors of observation.

A combination of two mols. of glyoxylic acid, one mol. of glycollic acid, and one mol. of water agrees much better with Doebner's experimental result than the composition of pure glyoxylic acid:  $C = 25.95$ ,  $H = 4.83$ , whereas  $2(C_2H_2O_3, H_2O) + C_2H_4O_3 + H_2O$  requires  $C = 25.90$ ,  $H = 5.03$  per cent.

It is therefore possible that the glyoxylic acid prepared by Doebner and used by him and Glass may have contained considerable quantities of glycollic acid, and as the glyoxylates possess a strong tendency to combine with glycollates (*Annalen*, 1856, 100, 10; 1863, 126, 133), the compounds described by Doebner and Glass as glyoxylates may have been such double salts.

If it is remembered that the action of chlorine on acetic acid produces at the same time, according to conditions, all three chlorinated acids, and that the boiling points of these acids are very near to each other, then it is clear that the preparation of pure dichloroacetic acid is by no means an easy operation. Doebner's potassium dichloroacetate may well have contained potassium monochloroacetate, from which glycollic acid would be formed.\*

Even if the dichloroacetate was pure, there may have been secondary reactions from which glycollates originated; at all events secondary reactions take place when a hot or boiling solution of silver dichloroacetate decomposes. From the numbers communicated by Beckurts and Otto, it follows that 55 grams of dichloroacetic acid, after neutralisation with silver carbonate and decomposition of the silver salt by boiling with water, gave 19.5 grams of potassium glyoxylate and 30 grams of potassium dichloroacetate. If no secondary products had been formed, 27.7 grams of potassium glyoxylate and 35.5 grams of potassium dichloroacetate ought to have been obtained. In other words, 22.5 per cent. of the dichloroacetic acid taken had been transformed in secondary reactions (*Ber.*, 1881, 14, 581). The nature of these secondary reactions is, however, not known.

Beckurts and Otto produce these numbers to show that an equal number of molecules of glyoxylates and dichloroacetates cannot be formed, on account of these secondary reactions.

At the same time, I ought to mention that in another paper (*Ber.*, 1881, 14, 1617), Beckurts and Otto make the following statement, which is logically opposed to what has just been related: "In the course of our studies on the behaviour of the halogen substitution products of the series  $C_nH_{2n}O_2$  at higher temperatures, or with boiling water, we observed that silver dichloroacetate is decomposed easily and completely ('schnell und glatt') into a mixture of an equal number of molecules

\* It is not improbable that Wallach's method may, under certain conditions, lead to the formation of ethyl chloroacetate (*Annalen*, 1873, 173, 301).

of glyoxylic and dichloroacetic acids." In other words, there are no secondary reactions.

I believe that the first of the two contradictory statements is correct.

Doebner's glyoxylic acid, mentioned before, was used by Doebner and Glass for the preparation of a number of salts. The description of the latter is very meagre; it is practically confined to a statement of the quantity of metal and that of water in a given weight of the salt. Neither characteristic reactions nor carbon and hydrogen determinations are given. Above all, the heated salts were not proved to be undecomposed glyoxylates. This ought to have been done, by reason of the facility with which glyoxylates decompose into oxalates and glycollates.

On account of these omissions, it is not possible to decide whether the salts called glyoxylates by Doebner and Glass were pure salts, isomeric with my glyoxylates, prepared from the acid obtained by the oxidation of ethyl alcohol, or double salts of my glyoxylates with glycollates and water.

I must leave it to Doebner and Glass to find, by a re-examination of their salts, the right answer to the above questions.

*Basic Calcium Glyoxylate,  $\text{Ca}(\text{OH})\cdot\text{C}_3\text{HO}_3\cdot\text{H}_2\text{O}$  (?).*

If a few drops of lime-water be added to a cold solution of calcium glyoxylate, a white turbidity, which dissolves again on shaking the mixture, will be produced. The liquid is now neutral or alkaline. A further addition of lime-water causes a permanent muddiness which, after a little time, becomes crystalline and settles down. But the clear liquid, after several minutes, becomes turbid again and produces a second precipitate. To a cold and clear solution of calcium glyoxylate, lime-water was added in such quantities that after shaking the mixture a permanent turbidity remained, and the whole then divided into three portions.

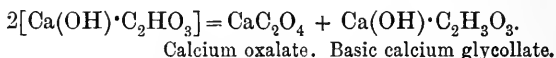
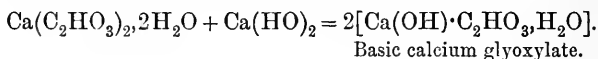
(1) To the first portion was added, without delay, some acetic acid, which rendered the liquid clear by dissolving all separated solid particles, and the liquid remained clear.

(2) After about one or two minutes, the second portion was acidified with acetic acid; the muddiness disappeared as in the first case, but it soon reappeared, and was then insoluble in acetic acid.

(3) About ten minutes after the foregoing experiments, the third portion was acidified with acetic acid. The muddiness remained, and the precipitated particles were not redissolved. These three experiments can be explained in the following manner.

The precipitate by lime-water in a solution of calcium glyoxylate is a basic salt, probably having the formula  $\text{Ca}(\text{OH}) \cdot \text{C}_2\text{HO}_3, \text{H}_2\text{O}$ . It is easily soluble in acetic acid, but sparingly so in water, and has an alkaline reaction.

Slowly at the ordinary temperature, but rapidly and completely at  $100^\circ$ , it decomposes into oxalate and basic glycollate:

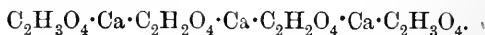


The basic calcium glycollate decomposes with water into calcium glycollate and calcium hydroxide. Immediately after its formation, the basic salt is converted by acids into soluble normal salt. This explains the first experiment.

A few minutes after its formation, the spontaneous decomposition of the basic salt commences, but proceeds only very slowly at the ordinary temperature, so that after 24 hours large portions of the basic salt are still unaltered.

If immediately after the commencement of the decomposition, and before the decomposition products have aggregated into larger particles, acetic acid is added, the entire precipitate will still dissolve, but the decomposition previously initiated in the alkaline liquid will proceed after acidification, and after a little time calcium oxalate, insoluble in acetic acid, will be precipitated. This behaviour reminds one of the latent action of light in photography or the observations of Becquerel that silver bromide is not decomposed by red light, but that it is thus decomposed after exposure for a moment to violet rays.

This is the explanation of the second experiment. If, however, an addition of acetic acid is made after the complete decomposition of a portion of the basic glyoxylate and formation of calcium oxalate, the precipitate will not dissolve. The unstable equilibrium of the particles in basic calcium glyoxylate prevents the quantitative analysis of the salt. Böttinger must have known the unstable nature of the salt, at least it appears from the precautions he took that he knew it, nevertheless, he has dried the precipitate caused by lime-water in a solution of calcium glyoxylate at  $110^\circ$ , and made a calcium determination with the dry residue. And from the result he calculated for the basic calcium glyoxylate the formula:



The solution of the normal calcium glyoxylate exhibits only a very slightly acid reaction, the solution of the basic salt is strongly alkaline. Therefore, a small quantity of lime-water added to a solution of the

neutral salt suffices to render the latter alkaline. Böttinger only added lime-water until the reaction of the solution of calcium glyoxylate just became alkaline. If he did so, then he can have obtained only a comparatively very small quantity of basic salt, which would spontaneously decompose in presence of the normal salt quite as well as it would if he had added sufficient lime-water for the complete precipitation of the normal calcium glyoxylate.

Böttinger's calcium determination was made on oxalate and glycollate not completely dried at  $110^{\circ}$ .

### *The Composition of Basic Calcium Glyoxylate.*

In order to ascertain approximately the composition of this salt, I have determined the quantity of lime-water which a known weight of calcium glyoxylate would require for its complete precipitation.

(1) A solution of 0.5 gram of calcium glyoxylate in 50 grams of hot water was allowed to cool to the ordinary temperature and then mixed with 45 c.c. of lime-water and placed overnight under a bell-jar by the side of pieces of potassium hydroxide.

The 45 c.c. of lime-water contained half the quantity of calcium present in 0.5 gram of calcium glyoxylate, namely, 0.045 gram. After 12 hours, a crystalline precipitate and fine crystals of normal calcium glyoxylate were observed on the sides and bottom of the beaker. If the formula of the basic salt given by Böttinger were correct, the whole of the calcium glyoxylate ought to have been converted into basic salt. But such was not the case. The filtrate from the precipitate and crystals gave, on concentration, additional quantities of normal salt.

The crystalline precipitate of basic salt was only partially soluble in acetic acid, calcium oxalate remaining undissolved. It produced with water and carbonic acid calcium carbonate and normal glyoxylate. From these experiments, I conclude that the precipitate caused by lime-water in a solution of calcium glyoxylate contains more calcium than is required by Böttinger's formula.

(2) A cold solution of 0.5 gram of calcium glyoxylate in 50 c.c. of water was mixed with 100 c.c. of lime-water which contained a little more calcium than was necessary for the complete precipitation of the glyoxylate. The filtrate of the precipitate produced a slight turbidity with carbonic acid.

Hence, one molecule of calcium hydroxide is sufficient for the conversion of one molecule of normal calcium glyoxylate into basic salt.

(3) A solution of 0.393 gram of calcium glyoxylate in 80 c.c. of water was mixed at the ordinary temperature with 35 c.c. of lime-water containing 0.035 gram of calcium and the copious precipitate

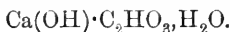
immediately collected on a filter. If the formula of the basic salt is assumed to be  $\text{Ca}(\text{OH}) \cdot \text{C}_2\text{HO}_3$ , then 0.393 gram of the normal salt would require 0.070 gram of calcium, corresponding with 70 c.c. of the lime-water, for conversion into basic salt. But only 35 c.c. of lime-water were added, and it follows that half of the normal glyoxylate must still be in solution.

To test the correctness of this conclusion, 35 c.c. of lime-water were added to the filtrate of the former precipitate, and the mixture boiled for several minutes to cause the decomposition of the basic salt formed into calcium oxalate and glycollate. The oxalate was collected on a filter and converted by the usual method into carbonate. The weight of the latter amounted to 0.075 gram.

If the filtrate from the first precipitation (115.2 c.c.) had still contained 0.196 gram of normal calcium glyoxylate, then the second precipitate by 35 c.c. of lime-water ought to have produced 0.128 gram of calcium oxalate corresponding with 0.087 gram of calcium carbonate. The experiment gave only 0.075. The difference between the last two numbers may be accounted for in the following manner.

The basic calcium glyoxylate obtained by the first addition of 35 c.c. of lime-water is to some extent spontaneously decomposed before it can be completely separated by filtration, and calcium hydroxide is one of the products of this decomposition (p. 1396). The calcium hydroxide set free in this manner will precipitate some of the calcium glyoxylate still in solution, and make its quantity less than 0.196 gram. Hence, the second precipitate obtained by 35 c.c. of lime-water must yield by decomposition a smaller quantity of calcium oxalate, and the latter a smaller quantity of carbonate than would be the case if the 115.2 c.c. of liquid had contained 0.196 gram of calcium glyoxylate.

The experiments described justify, in my opinion, the conclusion that the formula of the basic calcium glyoxylate given by Böttinger is not correct, and that the probable formula of the salt is



#### *Spontaneous Decomposition of Basic Calcium Glyoxylate at Common Temperatures.*

(1) A solution of 0.2455 gram of calcium glyoxylate in 50 c.c. of water was precipitated at 23° with 53 c.c. of lime-water. One hour afterwards, the mixture was acidified by acetic acid, the insoluble precipitate collected, and dried at 100°. The dry oxalate raised to a white heat left 0.038 gram of calcium oxide, corresponding with 0.087 gram of calcium oxalate. Therefore 61 per cent. of the glyoxylate taken had decomposed under the conditions of the experiment.

(2) A solution of 0.2145 gram of the same salt in 50 c.c. of water was mixed at  $23^{\circ}$  with 46 c.c. of lime-water and the mixture left for 24 hours, and at the end of this time acidified with acetic acid. The insoluble calcium oxalate gave 0.081 gram of calcium carbonate, which, when strongly heated, left 0.0465 gram of calcium oxide. Therefore 83 per cent. of the basic calcium glyoxylate taken had in 24 hours spontaneously decomposed into glycollate and oxalate.

(3) Calcium glyoxylate (0.2425 gram), dissolved in 50 c.c. of water, was mixed at  $23^{\circ}$  with 52 c.c. of lime-water and then left for 10 days. At the end of this time, the alkaline reaction of the solution having disappeared, it was acidified with acetic acid and the insoluble calcium oxalate collected and converted into carbonate weighing 0.09 gram, and the latter into oxide weighing 0.052 gram. Hence 82 per cent. of the glyoxylate taken had spontaneously decomposed.

Therefore, of 100 parts of calcium glyoxylate were decomposed : (1) after one hour, 61 parts ; (2) after 24 hours, 83.0 parts ; (3) after 10 days, 82.4 parts.

The spontaneous decomposition of basic calcium glyoxylate at the ordinary temperature appears to tend towards a certain limit. The concentration was the same in all cases : calcium glyoxylate, 1 part ; calcium hydroxide, 0.333 part ; water, 420.0 parts. At the boiling temperature, the decomposition is complete in a few minutes : 0.304 gram of calcium glyoxylate was dissolved in 50 c.c. of water, 65 c.c. of lime-water added, and the mixture boiled for about ten minutes. The alkaline liquid was then acidified with acetic acid and the insoluble oxalate collected on a filter. The weight of the calcium oxide obtained from the latter at higher temperatures was 0.077 gram, corresponding with 0.055 gram of calcium or 18 per cent. ; theory requires 18.0 per cent. (p. 1396).

In order to prove that the product of the decomposition of basic calcium glyoxylate, which is insoluble in acetic acid, is really calcium oxalate, 0.147 gram of the same, dried at  $100^{\circ}$ , was by careful heating converted into normal carbonate. The weight of the latter was 0.101 gram, which gives  $\text{Ca} = 27.4$  per cent., which is identical with the calculated value,  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ .

The only product of the decomposition of basic calcium glyoxylate which is soluble in acetic acid was proved in a former paper to be calcium glycollate (*Annalen*, 1856, 100, 8).

#### *Basic Zinc Glyoxylate.*

Considering the facility with which the basic calcium salt decomposes into oxalate and glycollate, the question arose whether the salt obtained by the precipitation of a solution of calcium glyoxylate with

zinc acetate is pure zinc glyoxylate or a mixture of the decomposition products of basic zinc glyoxylate.

In order to answer this question, a sample of basic zinc glyoxylate which had been prepared by the method mentioned and kept for several years was dissolved in the equivalent weight of dilute sulphuric acid and the clear solution evaporated under the receiver of an air-pump over concentrated sulphuric acid. The dry, crystalline residue could contain, besides glyoxylic acid and zinc sulphate, perhaps glycollic and oxalic acids. It was digested with alcohol, the solution filtered, mixed with water, and boiled for some time, and then examined for the acids mentioned. Oxalic acid was absent, whereas glyoxylic acid was present.

In order to make a complete analysis of the zinc glyoxylate, 1.5 grams of the calcium salt were precipitated by the addition of 3.4 grams of zinc acetate. The crystalline precipitate, which slowly separated, was collected after three days, washed with water, and dried in air over sulphuric acid under diminished pressure.

0.1955 gave 0.0920 ZnO.  $\text{Zn} = 37.80$ .

0.2605 (burnt with lead chromate) gave 0.1330  $\text{CO}_2$  and 0.0520  $\text{H}_2\text{O}$ .  $\text{C} = 13.93$ ;  $\text{H} = 2.23$ .

$\text{Zn}(\text{OH}) \cdot \text{C}_2\text{HO}_3, \text{H}_2\text{O}$  requires  $\text{Zn} = 37.71$ .  $\text{C} = 13.84$ ;  $\text{H} = 2.30$  per cent.

0.275 gram at  $100^\circ$  lost only 0.003 gram.

Another sample of the same preparation, which had been heated for some time at  $100^\circ$ , was dissolved in diluted sulphuric acid and examined for oxalic acid with a negative result.

A portion of the salt heated at temperatures varying from  $130^\circ$  to  $150^\circ$  lost 4.7 per cent, with the production of considerable quantities of zinc oxalate.

The basic zinc glyoxylate is colourless, nearly insoluble in water, but soluble in ammonia, acetic and hydrochloric acids.

### *Basic Manganous Glyoxylate.*

A cold and concentrated solution of calcium glyoxylate was mixed with an equivalent quantity of a concentrated solution of manganous acetate. In the course of a few days, a comparatively small quantity of flesh-coloured grains separated, which proved to be easily soluble in weak acetic acid.

0.311 (dried over sulphuric acid) gave 0.145  $\text{Mn}_2\text{O}_4$ .  $\text{Mn} = 33.6$ .

$\text{Mn}(\text{OH}) \cdot \text{C}_2\text{HO}_3, \text{H}_2\text{O}$  requires  $\text{Mn} = 33.5$  per cent.

The manganous and the zinc salts are of analogous composition.

*Basic Cupric Glyoxylate.*

A solution of crystallised cupric acetate in warm water, acidified with some acetic acid after it had cooled down to the ordinary temperature, was precipitated with calcium glyoxylate and the precipitate collected 24 hours after its formation.

The basic cupric glyoxylate is a light blue powder, insoluble in water, but soluble in acetic and hydrochloric acids. Ammonia caused the acetic acid solution of the salt to assume a dark blue colour, and calcium chloride did not produce any apparent change in the blue liquid. Therefore, oxalates are probably absent.

0.839 gram was dissolved in 0.490 gram of sulphuric acid, diluted with several times its weight of water, and the clear solution evaporated under diminished pressure over concentrated sulphuric acid. The residue digested with alcohol gave a slightly blue solution which gave the reactions of glyoxylic—but not those of oxalic acid.

0.376 (dried over sulphuric acid) gave 0.170 CuO.  $\text{Cu} = 36.1$ .

$\text{Cu}(\text{OH}) \cdot \text{C}_2\text{HO}_3, \text{H}_2\text{O}$  required  $\text{Cu} = 36.8$  per cent.

*Basic Lead Glyoxylate.*

A solution of calcium glyoxylate, mixed with one of lead acetate, produces a white, flocculent precipitate which, at the moment of its formation, is soluble in dilute acetic acid, but ten or fifteen minutes after its formation it becomes almost insoluble in the acid. The precipitate increases gradually for some time and assumes a crystalline appearance.

0.264 lost, at  $100^\circ$ ,  $0.008 \text{ H}_2\text{O} = 3.01$ .

0.413 gave 0.073 PbO and 0.213 Pb.  $\text{Pb} = 67.98$ .

$\text{Pb}(\text{OH}) \cdot \text{C}_2\text{HO}_3, \frac{1}{2}\text{H}_2\text{O}$  requires  $\text{H}_2\text{O} = 2.95$ ;  $\text{Pb} = 67.64$  per cent.

The salt is not pure, it undergoes spontaneously a partial decomposition during preparation into oxalate and glycollate, like the corresponding calcium salt; 1.295 grams of sulphuric acid were diluted with water, the solution added to 3.785 grams of the lead salt, and digested for two days. The liquid was then separated from the lead sulphate and a small quantity of free sulphuric acid precipitated from it by careful addition of barium carbonate. The filtrate from this precipitate, which gave the reactions of oxalic acid, could also contain glyoxylic and glycollic acids. In order to detect these acids, it was neutralised with calcium carbonate. The liquid portion could now contain calcium glyoxylate and glycollate and the solid portion calcium carbonate and oxalate. The solid portion was only partially soluble in acetic acid.

In a second experiment, 1.8 grams of very pure calcium glyoxylate were precipitated with basic lead acetate,  $\text{Pb}(\text{OH})\cdot\text{C}_2\text{H}_3\text{O}_2$ , at  $25^\circ$ . The copious precipitate was at first apparently amorphous, but became crystalline in the course of twelve hours. It consisted of tufts of fine needles, insoluble in water, but sparingly soluble in acetic acid. 4.1 grams of this salt were digested with 1.25 grams of sulphuric acid and water for two days, filtered, and the small excess of sulphuric acid in the filtrate removed with barium carbonate. The liquid could now contain glyoxylic acid and the products of the spontaneous decomposition of the lead glyoxylate. In order to isolate the latter, calcium carbonate was added, boiled, and filtered. The solid left on the filter could be the calcium carbonate taken in excess and calcium oxalate. It was well washed with acetic acid and water and finally dried at  $100^\circ$ .

0.117 gram of this residue gave 0.077 gram of calcium carbonate, corresponding with 26.3 per cent. of calcium; the formula  $\text{CaC}_2\text{O}_4\cdot\text{H}_2\text{O}$  requires 27.4 per cent. A difference of 1.1 per cent. between the experimental and the calculated amount of calcium is very considerable, nevertheless, I think, there can be no doubt that the precipitate was calcium oxalate.

The filtrate from the mixture of calcium oxalate and the excess of the calcium carbonate taken, gave, after suitable concentration, crystals of calcium glycollate and glyoxylate.

The spontaneous decomposition of the basic lead glyoxylate at common temperatures into glycollate and oxalate is, therefore, only partial, a considerable portion remaining unchanged. The extent of the decomposition has not been determined, and its cause has not been investigated. It is evidently dependent on the quantity of the base and the temperature. As the reaction is not reversible and takes place spontaneously, the entropy of the substances which take part in it must be increased.

It is worthy of notice that, as far as my observations go, only the basic salts of calcium and lead are decomposed in the manner indicated.

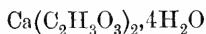
With regard to constitution, these basic salts of glyoxylic acid may be described in more than one way. They may be salts of the acid  $\text{C}_2\text{H}_2\text{O}_3$ , as described in this paper, or salts of the acid  $\text{C}_2\text{H}_4\text{O}_4$ , and their formation may be due to the presence of two equivalents of hydroxyl.

But if it is remembered that by the adoption of the formula  $\text{C}_2\text{H}_4\text{O}_4$  one molecule of water appears in all principal reactions as an unnecessary appendix, that is to say, all the chief reactions can be described by the aid of the formula  $\text{C}_2\text{H}_2\text{O}_3$  in a more simple manner than by the formula  $\text{C}_2\text{H}_4\text{O}_4$ , I consider the formula used in this paper sufficiently justified.

*Calcium Glycollate.*

There appears to exist some confusion with regard to the water of crystallisation of calcium glycollate. This has been caused by Böttinger, who asserts (*Annalen*, 1879, 198, 227, 228) that calcium glycollate always crystallised from dilute solutions with four molecules of water.

Not in one, like Böttinger, but in eight determinations I found the water of crystallisation of calcium glycollate, dried in air at the ordinary temperature, to be 29.4 per cent. (*Annalen*, 1873, 166, 116, 119, 122), whilst the calculated value for the formula



is 27.48 per cent., or 2 per cent. less. The formula  $\text{Ca}(\text{C}_2\text{H}_3\text{O}_3)_2 \cdot 4\frac{1}{2}\text{H}_2\text{O}$  requires  $\text{H}_2\text{O} = 29.8$  per cent., and this is much nearer my own observations than Böttinger's number. The agreement becomes closer with purer specimens of the salt. The purest salt I examined gave 29.4 instead of 29.8 per cent. of water. Therefore calcium glycollate crystallised from water at common temperatures has the formula  $2[\text{Ca}(\text{C}_2\text{H}_3\text{O}_3)_2] \cdot 9\text{H}_2\text{O}$ . In air, it loses a portion of this water, the amount depending on the temperature and the humidity of the atmosphere. In dry air, over sulphuric acid, it loses exactly one-third of its water of crystallisation and becomes converted into  $\text{Ca}(\text{C}_2\text{H}_3\text{O}_3)_2 \cdot 3\text{H}_2\text{O}$ . At  $120^\circ$ , all the water is eliminated.

From these facts, it follows that calcium glycollate will contain variable quantities of water according to the temperature and the humidity of the air in which it has been dried.

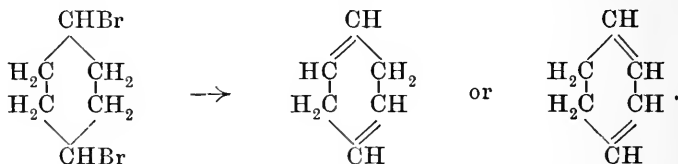
CXLII.— $\Delta^{1:3}$ -Dihydrobenzene.

By ARTHUR WILLIAM CROSSLEY.

SOME little time ago experiments were described which had for their object the preparation of dihydrobenzene from dihydroresorcin (Crossley and Haas, *Trans.*, 1903, 83, 494). The hydrocarbon obtained was not pure, being contaminated with tetrahydrobenzene, but from an examination of its properties there was no doubt that it was different from any previously described dihydrobenzene, and was, as then supposed and now corroborated, in reality  $\Delta^{1:3}$ -dihydrobenzene. Further work, described in the first part of the experimental portion of this communication, showed that it is apparently impossible to obtain

absolutely pure dihydrobenzene from dihydroresorcin; therefore another method was sought, and a possible one seemed to consist in the removal of the elements of hydrogen bromide from 1:2-dibromohexahydrobenzene ("dibromotetrahydrobenzene").

The first chemist to prepare dihydrobenzene was von Baeyer, who obtained it by the action of quinoline on 1:4-dibromohexahydrobenzene (*Annalen*, 1894, 278, 94), and who pointed out (*ibid.*, p. 113) that the resulting hydrocarbon may have one of two formulæ, according to the way in which the elements of hydrogen bromide are removed:



A similar objection cannot be urged against the hydrocarbon obtained by the action of quinoline on 1:2-dibromohexahydrobenzene, where the removal of the elements of hydrogen bromide can only give rise to one of the two dihydrobenzenes theoretically capable of existence:



There are, however, other possibilities, which are discussed on p. 1405.

As regards 1:2-dibromohexahydrobenzene, there are two recorded statements concerning the behaviour of reagents which remove hydrogen bromide. Baeyer (*ibid.*, p. 108) maintains that "when 1:2-dibromohexahydrobenzene is acted on with quinoline or with zinc dust and acetic acid, tetrahydrobenzene is regenerated," and Fortey (*Trans.*, 1898, 73, 948) states that "1:2-dibromohexahydrobenzene is readily acted on by alcoholic potash, yielding dihydrobenzene."

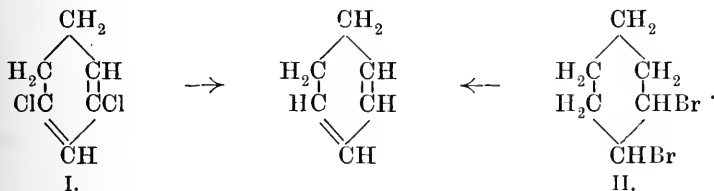
In view of these somewhat contradictory statements, it seemed doubly worth while to investigate the action of both alcoholic potash and quinoline on 1:2-dibromohexahydrobenzene. This bromo-compound was therefore prepared by the method used by von Baeyer (*ibid.*, p. 100), starting with the synthesis of *n*-pimelic acid, and acted on with a saturated solution of potassium hydroxide in absolute alcohol, when the main reaction consists in the removal of one bromine atom as hydrogen bromide and the replacement of the second bromine atom by an ethoxyl group, thus giving rise to 1-ethoxy- $\Delta^2$ -tetrahydro-

benzene,  $\text{CH}_2 \begin{array}{c} \text{CH}_2 \cdot \text{CH} \cdot \text{O} \cdot \text{C}_2\text{H}_5 \\ \text{CH}_2 \text{-----CH} \end{array} \text{CH}$ , the yield of which is 77 per cent. The constitution of this substance is established by the experiments described on p. 1416.

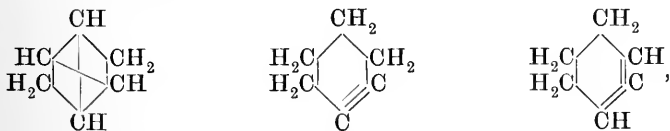
The product is a colourless, refractive liquid boiling at  $154.5^\circ$  and possessing a pungent odour of peppermint. During the reaction which leads to the production of ethoxytetrahydrobenzene, a small quantity of dihydrobenzene is formed, but it is  $\Delta^{1:3}$ -dihydrobenzene, giving the solid dibromide melting at  $108^\circ$ , and is not, therefore, the same hydrocarbon as described by Fortey, which gave a solid tetrabromide melting at  $184^\circ$ . Fortey does not give any experimental data concerning the dihydrobenzene obtained by the action of alcoholic potash on 1:2-dibromohexahydrobenzene, and it is therefore to be presumed that this investigator considered it to be identical with the dihydrobenzene described in an earlier part of her paper.

The sole product of the action of quinoline on 1:2-dibromohexahydrobenzene is  $\Delta^{1:3}$ -dihydrobenzene, a colourless, highly refractive liquid boiling at  $81.5\text{--}82^\circ$ , and in every respect identical with the hydrocarbon obtained from dihydroresorcin by the series of reactions already described (Trans., 1903, 83, 503).

In discussing the constitution of this hydrocarbon, the first point to be borne in mind is that the same substance results from the reduction of 3:5-dichloro- $\Delta^{2:4}$ -dihydrobenzene (I) and from 1:2-dibromohexahydrobenzene (II) by the elimination of the elements of hydrogen bromide:



There would seem therefore to be but one possibility, namely, the formation of  $\Delta^{1:3}$ -dihydrobenzene in both cases; for substances having the following formulæ:

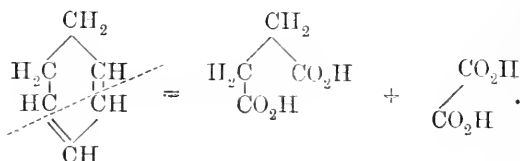


may be excluded, as, although theoretically obtainable from 1:2-dibromohexahydrobenzene, their production from 3:5-dichloro- $\Delta^{2:4}$ -dihydrobenzene cannot readily be explained. It must also be remembered that 1:1-dimethyl- $\Delta^{2:4}$ -dihydrobenzene has been prepared from

3:5-dichloro-1:1-dimethyl- $\Delta^{2:4}$ -dihydrobenzene (Trans., 1902, 81, 832) and that the constitution of these substances has been established.

If, then, the hydrocarbon is  $\Delta^{1:3}$ -dihydrobenzene, there are several properties and transformations which it should undergo, and which would leave no doubt as to its constitution.

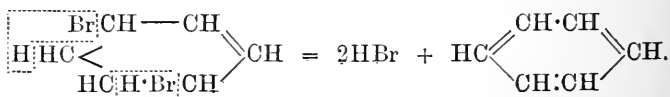
In the first place, it should give, on oxidation, oxalic and succinic acids, as, in fact, it does:



Potassium permanganate has been the usual oxidising agent employed in such instances, but, although it gives highly satisfactory results with dimethyldihydrobenzene (Trans., 1902, 81, 836), it does not do so in the present case on account of the difficulty of separating the succinic acid from the potassium sulphate formed on acidifying the oxidation product with sulphuric acid. As neither oxalic nor succinic acid is readily further oxidised by nitric acid, an attempt to use this reagent was made with surprisingly satisfactory results; for there was no difficulty, even when using so small a quantity of the hydrocarbon as 2 grams, in isolating both oxalic and succinic acids. The latter acid was identified by means of the melting points of its anhydride, anilic acid, and anil.

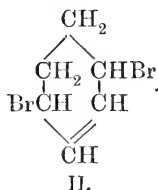
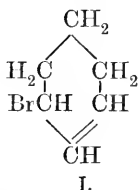
A special search was made for malonic acid, which would result from the oxidation of the isomeric dihydrobenzene, but not a trace could be detected.

In the second place, if the hydrocarbon is  $\Delta^{1:3}$ -dihydrobenzene, then it contains double bonds in the position dealt with by Thiele in his theory of partial saturation (*Annalen*, 1899, 306, 87), and it should therefore be characterised by only adding on 1 molecule of either bromine or hydrogen bromide (compare 1:1-dimethyl- $\Delta^{2:4}$ -dihydrobenzene, Trans., 1902, 81, 825). This anticipation is confirmed experimentally, bromine giving rise to 1:4-dibromo- $\Delta^2$ -tetrahydrobenzene, which is a beautifully crystalline solid melting at  $108^\circ$  and decomposing with evolution of hydrogen bromide at  $170^\circ$ . That this substance is in reality a dibromodihydrobenzene is conclusively proved by the fact that on treatment with quinoline it loses 2 molecules of hydrogen bromide yielding benzene:



This is probably the same decomposition which this substance undergoes on being heated at  $170^\circ$ .

Hydrogen bromide acts on  $\Delta^{1:3}$ -dihydrobenzene giving rise to 1-bromo- $\Delta^2$ -tetrahydrobenzene, a colourless liquid boiling at  $74^\circ/28$  mm. In view of the similar constitutions of mono- (I) and di-bromotetrahydrobenzenes (II), it is of interest to note their different behaviour towards bromine in chloroform solution. The latter is quite unaffected, whereas monobromotetrahydrobenzene absorbs bromine extremely slowly. It is impossible to say whether this takes place originally by the process of addition or substitution, for after 3 hours the amount of bromine used up is considerably less than two atoms and at the end of 6 hours considerably more than two atoms :



The explanation of this difference in behaviour is doubtless to be sought in the protective influence of the bromine atoms on the double linking, for in dibromotetrahydrobenzene this bond is guarded on both sides by bromine atoms, whereas in monobromotetrahydrobenzene protection is afforded only on one side.

Lastly, and of great importance in support of the constitution of  $\Delta^{1:3}$ -dihydrobenzene, are the physical data which Dr. Perkin, sen., has very kindly determined and which are to be found in the experimental part of this communication.

It becomes necessary, in conclusion, to survey briefly the chemistry of the dihydrobenzenes, because previously recorded work on  $\Delta^{1:3}$ -dihydrobenzene does not agree with the work herein described.

As already mentioned, Baeyer's hydrocarbon might be a mixture of the two possible dihydrobenzenes, but Baeyer definitely states (*Annalen*, 1894, 278, 113) that he believed it to be homogeneous, although unable to decide whether the double bonds were in the 1:3- or 1:4-position. The hydrocarbon obtained by Fortey (*Trans.*, 1898, 73, 948) would appear to be identical with the above.

Baeyer's hydrocarbon, on treatment with bromine, gave beautiful crystals of the tetrabromide melting at  $184^\circ$  and an oil, which he considered might be the *cis*-form. On account of this statement, and also because the hydrocarbon gave a violet-red coloration with alcoholic sulphuric acid, Markownikoff (*Annalen*, 1898, 302, 33) thought that Baeyer's substance was a mixture. Moreover, Markownikoff did not believe that the bromide melting at  $184^\circ$  was homogeneous, because by

repeated crystallisation he obtained fractions of different melting point ( $184$ — $187^\circ$ ), and also because, when a crystal melting at  $186$ — $187^\circ$  was kept for 2 hours at a temperature of  $195$ — $200^\circ$ , it afterwards melted at  $180$ — $182^\circ$ . This is not a surprising result when the sensitive nature of the substance is taken into account. It would, in fact, be more surprising if some slight decomposition had not taken place, quite enough to alter the melting point by a few degrees.

Markownikoff prepared dihydrobenzene by treating with quinoline the various fractions of dichlorohexahydrobenzene obtained by the action of chlorine on hexahydrobenzene isolated from petroleum, and presumed that the more volatile fraction ( $190$ — $192^\circ$ ) was 1 : 3-dichlorohexahydrobenzene and that the less volatile fraction ( $196$ — $198^\circ$ ) was 1 : 4-dichlorohexahydrobenzene. The hydrocarbons from both these fractions gave, on treatment with bromine in chloroform solution, the tetrabromide melting at  $184^\circ$  together with more or less liquid, in the latter case the product being almost entirely liquid. Markownikoff concluded that the hydrocarbons were mixtures of the two possible dihydrobenzenes, the former consisting principally of  $\Delta^{1:3}$ -dihydrobenzene and the latter being mainly  $\Delta^{1:4}$ -dihydrobenzene, but he was unable to give an opinion as to whether the mixture was a result of the impurity of the initial material (dichlorohexahydrobenzene) or whether it was due to the elimination of the elements of hydrogen chloride in different directions.

Despite the fact that he does not put forward any direct evidence as to the constitution or homogeneity of the dichlorohexahydrobenzenes which he employed, Markownikoff concluded that the hydrocarbon giving principally the solid tetrabromide melting at  $184^\circ$  was  $\Delta^{1:3}$ -dihydrobenzene and the one giving the liquid bromide was  $\Delta^{1:4}$ -dihydrobenzene.

One fact recorded by Markownikoff (*ibid.*, p. 34) is extremely interesting; he states that from the fraction of dichlorohexahydrobenzene boiling at  $194$ — $196^\circ$  he obtained a hydrocarbon which gave an oily bromide, from which there slowly separated crystals melting at  $108^\circ$  and decomposing at  $170^\circ$ . No analysis or further description of this substance is given, so it is impossible to say whether it was a di- or tetra-bromide; but, inasmuch as the melting and decomposing points are identical with those of 1 : 4-dibromo- $\Delta^2$ -tetrahydrobenzene (see page 1421), it would appear that Markownikoff actually had this substance in his possession.

Markownikoff's experience entirely corroborates that of the author, for although 1 : 4-dibromo- $\Delta^2$ -tetrahydrobenzene crystallises with facility when once it has been obtained in the solid form, it does not separate at all readily from a liquid when mixed with other substances (see page 1421). When it was originally obtained (Trans., 1903,

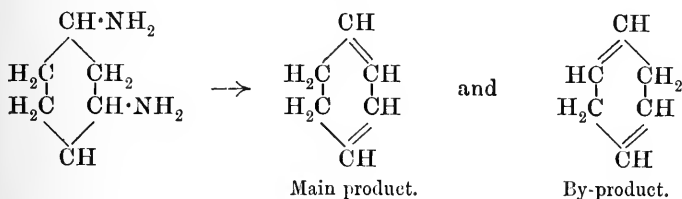
83, 504), it crystallised only after six months, because it was then mixed with 1:2-dibromohexahydrobenzene.

In a former paper (Crossley and Haas, *Trans.*, 1903, 83, 498), it was stated that, if further experiments supported the work then described, the hydrocarbon obtained from dihydroresorcin would be  $\Delta^{1:3}$ -dihydrobenzene and the hydrocarbon giving the solid tetrabromide melting at  $184^\circ$  would be  $\Delta^{1:4}$ -dihydrobenzene.

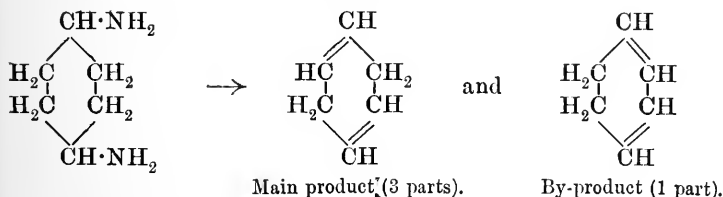
This supposition, which is proved to be correct by the work now described, elicited a direct contradiction from Harries and Antoni (*Annalen*, 1903, 328, 88),\* who believe that Markownikoff's conclusions are entirely supported by their work. This seems to be founded on evidence which, as in Markownikoff's case, is misleading.

The method of preparation adopted by Harries and Antoni consists in the dry distillation of the phosphates of certain cyclic diamines, whereby two molecules of ammonia are split off with the production of a doubly unsaturated hydrocarbon. The two diamino-hexahydrobenzenes with the amino-groups in the 1:3- and 1:4-positions were employed, and are supposed to yield 1:3- and 1:4-dihydrobenzenes respectively, but not in a pure condition, because the elimination of ammonia takes place, in both cases, in the two possible ways:

*Reaction 1.*



*Reaction 2.*



This conclusion is founded solely on the behaviour of these hydrocarbons towards bromine, for Harries and Antoni found that the hydrocarbon obtained by the first reaction gave, on treatment with

\* (*Ibid.*, p. 102.) Die Auffassung von Crossley, dass das Cyclohexadien-(1:4) mit Brom das bei  $184^\circ$  schmelzende Tetrabromide liefert, ist durch die von uns mitgetheilten Beobachtungen widerlegt.

bromine, principally the solid tetrabromide melting at  $184^{\circ}$ , whereas the hydrocarbon from the second reaction gave mainly a liquid bromide with very little of the solid (m. p.  $184^{\circ}$ ). Hence their assumption presupposes that  $\Delta^{1:3}$ -dihydrobenzene gives rise to the solid tetrabromide, and  $\Delta^{1:4}$ -dihydrobenzene gives the oily bromide. Surely if any deduction is to be drawn from our present knowledge of the behaviour of double linkings towards bromine, it would be that  $\Delta^{1:4}$ -dihydrobenzene would directly absorb four atoms of bromine, whilst  $\Delta^{1:3}$ -dihydrobenzene, containing as it does the double bonds in the "Thiele position," would only add on two atoms of bromine.

Harries and Antoni (*ibid.*, p. 106) state that when a weighed quantity of either of the mixtures of hydrocarbons obtained by the two foregoing reactions is treated with bromine in chloroform solution, exactly four atoms of bromine are absorbed; so that these authors have apparently never had  $\Delta^{1:3}$ -dihydrobenzene in their possession, for this compound, as is shown in the experimental part of this communication (see page 1421), only absorbs two atoms of bromine per molecule.

Harries and Antoni state that "during the treatment with bromine some hydrogen bromide is evolved and the product in both cases consisted of crystals melting at  $184^{\circ}$ , together with more or less oil," and further, "it is difficult to say whether this oil is produced by the presence of the second variety of dihydrobenzene or whether it is due to a resinification (*Verhartung*) of the pure dihydrobenzene, caused by the hydrogen bromide liberated during bromination." "The reaction is never quantitative." Yet the composition of the mixture of hydrocarbons obtained by the foregoing reactions is ascertained solely from a consideration of the varying amounts of solid and oily bromides produced.

From the author's experience, it would appear that the supposition of Harries and Antoni that the oil is produced by some secondary reaction is the correct one, for from pure  $\Delta^{1:3}$ -dihydrobenzene a quantitative yield of the solid dibromide is never obtained. This is not surprising when it is remembered what an extremely sensitive substance dihydrobenzene is, and also the great chemical reactivity of bromine. The best yield of dibromotetrahydrobenzene is obtained by working with very small quantities of  $\Delta^{1:3}$ -dihydrobenzene, taking care to add the bromine very slowly and keeping the whole well cooled. If these precautions are not taken, the amount of solid obtained is very small, and it is only after a long time that the crystals form at all. In one case where a quantity of the hydrocarbon had been treated with bromine without taking any particular precautions, the resulting liquid did not deposit crystals for two months; but then, on sowing with a crystal of the dibromide melting

at 108°, rapid solidification took place. The fact that this dibromide does not readily separate may be the reason why its identity has not been previously established.

Harries and Antoni (*ibid.*, p. 91) lay stress on oxidation experiments as a means of elucidating the constitution of their hydrocarbons; they oxidised the substances obtained by the reactions 1 and 2 with potassium permanganate, and isolated oxalic and succinic acids from the first, and small quantities of succinic and malonic acids from the second; in this case, the hydrocarbon appeared to be almost entirely decomposed. No information at all is given as to the amount of these acids obtained or how they were isolated, or whether they were merely identified as already described by Harries (*Ber.*, 1902, 35, 1173), the oxalic acid as its phenylhydrazine salt (m. p. 184°) and the succinic acid by the pyrrole reaction. The present author experienced no difficulty in isolating appreciable quantities of both oxalic and succinic acids from the oxidation of  $\Delta^{1:3}$ -dihydrobenzene (see page 1423) when using nitric acid as oxidising agent.

As Harries and Antoni assume that their hydrocarbons are both mixtures of the two possible dihydrobenzenes, oxalic, succinic, and malonic acids should result from the oxidation of either, and without further details it would seem to be impossible to draw any very definite conclusions from their oxidation experiments.

#### EXPERIMENTAL.

In a previous communication (Trans., 1903, 83, 504), it was mentioned that, when the mixture of hydrocarbons obtained by the reduction of 3:5-dichloro- $\Delta^{2:4}$ -dihydrobenzene was treated with bromine, there resulted a slightly coloured liquid, which did not decompose when left in a desiccator over calcium chloride, and from which crystals of 1:4-dibromo- $\Delta^2$ -tetrahydrobenzene (dibromodihydrobenzene) slowly separated. After four months, the formation of crystals had ceased, and in order to obtain evidence as to the nature of the residual liquid, which was thought to be 1:2-dibromohexahydrobenzene ("dibromotetrahydrobenzene"), it was heated in a distillation flask with freshly distilled quinoline. The temperature of the mixture was slowly raised, during the course of an hour, to 170°, when a decided reaction set in, and after this had abated the thermometer was raised out of the liquid and all distilled over up to a temperature of 95°. The resulting hydrocarbon still contained bromine, so it was again distilled from quinoline and fractionated several times over metallic sodium, when it was found to boil at 80—80.5°/755 mm.

When concentrated sulphuric acid was added to a solution of this

hydrocarbon in alcohol, a raspberry-red coloration was at first produced, rapidly turning to bluish-violet.

Determinations of the bromine absorptive capacity of the hydrocarbon gave the following results:

1.1127 absorbed 1.1600 Br. Molecular absorption = 83.4.

1.0710 absorbed 1.1300 Br. Molecular absorption = 84.4.

$C_6H_8$  requires  $Br_2 = 160$ .

These numbers show that the hydrocarbon is a mixture of dihydrobenzene and benzene in approximately equal quantities, and the presence of benzene was proved by the production of nitrobenzene on treatment with a mixture of nitric and sulphuric acids.

The original residual liquid must therefore have consisted of the dibromo-additive compounds of dihydro- and tetrahydro-benzenes, as the elimination of hydrogen bromide from these substances would give rise respectively to benzene and dihydrobenzene. The 1:4-dibromo- $\Delta^2$ -tetrahydrobenzene melting at  $108^\circ$  had not then completely separated, despite the fact that the liquid had been left for four months; and at a later stage of the inquiry it was proved that this substance is very readily soluble in 1:2-dibromohexahydrobenzene, and although it separates to some extent on cooling in a freezing mixture, it immediately redissolves on attaining the ordinary atmospheric temperature.

On evaporating the chloroform used in the above bromine absorptions, the residual liquid rapidly deposited crystals of 1:4-dibromo- $\Delta^2$ -tetrahydrobenzene melting at  $108^\circ$ .

These experiments seemed to point to the possibility of ultimately obtaining  $\Delta^{1:3}$ -dihydrobenzene in a pure condition from dihydroresorcin, for they clearly show that the dihydrobenzene obtained by the action of nascent hydrogen on dichlorodihydrobenzene is identical with that produced by the elimination of the elements of hydrogen bromide from 1:2-dibromohexahydrobenzene, and the only doubtful point to be cleared up was, whether it would be possible to separate completely 1:4-dibromo- $\Delta^2$ -tetrahydrobenzene from 1:2-dibromohexahydrobenzene by the process of fractional distillation.

An additional 35 grams of the mixture of hydrocarbons obtained by treating dichlorodihydrobenzene with sodium in moist ethereal solution was then prepared in the manner already described (Trans., 1903, 83, 503). It was at once converted into the bromo-additive compound and this allowed to remain for some months, when the filtrate from the separated crystals (m. p.  $108^\circ$ ) was distilled in a vacuum, and gave the following fractions:

111—114° = 6.7 grams.    114—115° = 43 grams.

115—117° = 15 grams.    117—130° = 15 grams.

These fractions were then left for a further period of three months, but crystals separated only from the fraction boiling at 117—130°.

The portions boiling at 114—115° and 115—117° were then repeatedly redistilled, when 37 grams of a clear, colourless, highly refractive liquid were obtained, distilling constantly at 114.5°/24 mm. without any sign of decomposition. Unfortunately, the constancy in the boiling point was the only criterion of the purity of this substance, as the differences in the analytical numbers of dibromotetrahydrobenzene and dibromohexahydrobenzene are too small to allow of any conclusions being drawn. Moreover, the boiling point of dibromohexahydrobenzene, as given by Baeyer (*Annalen*, 1894, 278, 108) and Markownikoff (*Annalen*, 1898, 301, 29), was no help; but the boiling point is in close agreement with that of pure dibromohexahydrobenzene (116°/29 mm.), determined subsequently to the above experiments (see page 1415).

The 37 grams of liquid were then treated with quinoline as described on p. 1416. After fractionation over sodium, the product boiled constantly at 81.5° and had a sp. gr. 0.8328 at 15°/15°, that of pure 1:3-dihydrobenzene being 0.8377 at 15°/15°. When dissolved in alcohol and treated with concentrated sulphuric acid, it gave a momentary red coloration turning to an intense bluish-violet, which remained permanent. A bromine absorption gave the following numbers:

1.0004 absorbed 1.7920 Br. Molecular absorption Br = 143.3.

$C_6H_8$  requires Br<sub>2</sub> = 160.

On evaporating the chloroform, the residue solidified almost completely and consisted of 1:4-dibromo- $\Delta^2$ -tetrahydrobenzene melting at 108°. The sp. gr. and bromine absorption show that this specimen consisted of almost pure  $\Delta^{1:3}$ -dihydrobenzene, but as there did not seem to be any ready means of ascertaining whether the 1:2-dibromohexahydrobenzene, prepared as above, was absolutely pure, further experiments in this direction were not made.

*Action of Sodium in Amyl-alcoholic Solution on 3:5-Dichloro- $\Delta^{2:4}$ -dihydrobenzene.*

The action of sodium in amyl-alcoholic solution on dichlorodihydrobenzene was investigated in the hope of obtaining a homogeneous substance: and it was expected, in view of the strong reducing properties of this reagent, that hexahydrobenzene would result. This is not, however, the case, as the following experiments prove.

Ten grams of dichlorodihydrobenzene were dissolved in 150 c.c. of amyl alcohol, the whole heated to boiling in a flask attached to a con-

denser, the end of which was connected with an absorption apparatus containing amyl alcohol, and 15 grams of sodium gradually added. When all the sodium had dissolved, the amyl alcohol in the absorption apparatus was added to the contents of the flask and the whole distilled, using a fractionating column, when small quantities of a liquid with a lower boiling point than amyl alcohol passed over. The distillates from several such experiments were united and repeatedly fractionated over sodium, when a liquid was obtained boiling at  $79.5-80^\circ$ . With alcoholic sulphuric acid, it slowly acquired a pink colour, and a bromine absorption gave the following result:

1.0742 absorbed 0.602 Br. Molecular absorption,  $\text{Br} = 44.8$ .

$\text{C}_6\text{H}_8$  requires  $\text{Br}_2 = 160$ .

In order to separate the saturated from the unsaturated material present, 10 grams of this hydrocarbon were dissolved in dry ether and bromine gradually added until no more was absorbed, taking care that the temperature did not rise above  $0^\circ$ . The whole was then carefully fractionated, using a column, and the portion boiling between  $60^\circ$  and  $80^\circ$  was redistilled over metallic sodium, when 6 grams of a liquid boiling constantly at  $80.5-81^\circ$  were obtained, which consisted of nearly pure benzene.

0.1569 gave 0.5256  $\text{CO}_2$  and 0.1208  $\text{H}_2\text{O}$ .  $\text{C} = 91.37$ ;  $\text{H} = 8.55$ .

$\text{C}_6\text{H}_6$  requires  $\text{C} = 92.30$ ;  $\text{H} = 7.70$  per cent.

The liquid had a sp. gr. 0.8733 at  $15^\circ/15^\circ$  (benzene has a sp. gr. 0.8786 at  $15^\circ/15^\circ$ ), and on warming with a mixture of fuming nitric acid and concentrated sulphuric acid gave *m*-dinitrobenzene (m. p.  $90^\circ$ ).

The substance produced in the above reaction, which does not absorb bromine, is not therefore hexahydrobenzene but benzene. Its formation is readily accounted for by supposing that sodium amyl-oxide is sufficiently alkaline in nature to remove the elements of hydrogen chloride from dichlorodihydrobenzene, and no doubt this reaction also takes place to a certain extent when sodium in moist ethereal solution acts on dichlorodihydrobenzene.

#### *Preparation of 1:2-Dibromohexahydrobenzene.*

Tetrahydrobenzene was prepared by the directions given by von Baeyer (*Annalen*, 1894, 278, 100), and the following description contains a few supplementary practical details.

Ethyl pentamethylenetetracarboxylate (440 grams), boiling at  $225-290^\circ/100$  mm., was obtained by working up 1500 grams of ethyl malonate and 500 grams of trimethylene bromide.

For the saponification of this ethereal salt, 50 c.c. were mixed with

70 c.c. of concentrated sulphuric acid and 70 c.c. of water and the whole heated to boiling without attaching the containing flask to a condenser; bumping is entirely avoided by making use of a Babo's funnel. As soon as sulphur dioxide was given off (35—40 minutes), 200 c.c. of water were added and the whole left overnight, when the majority of the pimelic acid crystallised out. This was separated by filtration, the filtrate extracted five times with ether, and the solid residue obtained on evaporating off the solvent added to the pimelic acid which had previously separated. After one crystallisation from benzene, the acid melted at 103—105°. In this way, 143 grams of pimelic acid were obtained from 440 grams of ethyl pentamethylene-tetracarboxylate.

Two hundred and sixty-five grams of pimelic acid gave 90 grams of ketohexahydrobenzene (pimelinketone), boiling at 155—156°, after purification by means of sodium hydrogen sulphite. From this amount of ketohexahydrobenzene there were obtained 73 grams of hydroxyhexahydrobenzene, boiling at 160.5°/757 mm. and solidifying at the ordinary temperature to needle-shaped crystals (compare Markownikoff, *Annalen*, 1898, 302, 21); and in addition 8 grams of ketohexamethylenepinacone, crystallising from light petroleum in slender, glistening needles melting at 129—130° (compare Zelinsky, *Ber.*, 1901, 34, 2801). The above quantity of hydroxyhexahydrobenzene gave 95 grams of bromohexahydrobenzene boiling at 69—70°/29 mm., which on treatment with alcoholic potassium hydroxide (compare Markownikoff, *ibid.*, p. 27) yielded 36 grams of pure tetrahydrobenzene boiling at 84°/768 mm.

1:2-Dibromohexahydrobenzene is a clear, colourless, highly refractive liquid boiling at 116°/29 mm.; it cannot be distilled in air, as it evolves hydrogen bromide, nor can it be kept exposed in air without becoming very dark and decomposing; but in a dry atmosphere it remains unchanged for months (compare Baeyer, *ibid.*, p. 108; Markownikoff, *ibid.*, p. 29; Fortey, *Trans.*, 1898, 73, 948).

*Action of Alcoholic Potash on 1:2-Dibromohexahydrobenzene.*

Fifteen grams of 1:2-dibromohexahydrobenzene were gradually added to 100 c.c. of a boiling solution of alcoholic potassium hydroxide, when a vigorous reaction took place and potassium bromide separated. After continuing the heating for three hours, the major portion of the alcohol was distilled off (residue from this distillation = A) and poured into water, when an oil separated, which, after drying over calcium chloride, weighed 2 grams. On distillation, only a few drops passed over between 78° and 85°; the temperature then rose rapidly to 150°, and the residue distilled at 154.5° and proved to be identical

with the ethoxyl compound described below and to which it was added.

The portion boiling at  $78-85^\circ$  contained  $\Delta^{1:3}$ -dihydrobenzene, for it gave with bromine 1 : 4-dibromo- $\Delta^2$ -tetrahydrobenzene (m. p.  $108^\circ$ ) and with alcoholic sulphuric acid a blood-red coloration, turning to deep bluish-violet (see page 1419).

The above residue (A) was poured into water, the whole extracted with ether, the ethereal solution washed with water, dried with anhydrous sodium carbonate, and the ether evaporated. The residue, weighing 4 grams, boiled constantly at  $154.5^\circ$ .

0.1156 gave 0.3218  $\text{CO}_2$  and 0.1162  $\text{H}_2\text{O}$ .  $\text{C} = 75.92$  ;  $\text{H} = 11.16$ .

$\text{C}_8\text{H}_{14}\text{O}$  requires  $\text{C} = 76.19$  ;  $\text{H} = 11.11$  per cent.

1-Ethoxy- $\Delta^2$ -tetrahydrobenzene,  $\text{CH}_2 \begin{array}{c} \text{CH}_2 \cdot \text{CH} \cdot \text{O} \cdot \text{C}_2\text{H}_5 \\ \text{CH}_2 \text{-----} \text{CH} \end{array} \text{CH}$ , is a clear, colourless liquid boiling at  $154.5^\circ$  and possessing a pungent odour of peppermint, yet somewhat resembling that of ethyl benzoate. It is characterised by the colour reaction with alcoholic sulphuric acid, which at first produces an evanescent brownish-red colour, followed by the immediate separation of a green solid. With the further addition of sulphuric acid, the colour becomes violet and finally deep indigo-blue. When a chloroform solution of bromine is added to a solution of this ethoxyl compound in the same solvent, the colour of the bromine is rapidly discharged.

0.5120 absorbed 0.6625 Br. Molecular absorption,  $\text{Br} = 163$ .

$\text{C}_8\text{H}_{14}\text{O}$  requires  $\text{Br}_2 = 160$ .

On evaporating the chloroform, there remained a slightly coloured, pungent-smelling liquid, which did not solidify, and which decomposed, on distillation in air, with the evolution of hydrogen bromide. The presence of an ethoxyl group was shown by a Zeisel determination, carried out according to the instructions given by Perkin (Trans., 1903, 83, 1367).

0.3180 gave 0.5660 AgI.  $-\text{OC}_2\text{H}_5 = 34.09$ .

$\text{C}_8\text{H}_{14}\text{O}$  requires  $-\text{OC}_2\text{H}_5 = 35.70$  per cent.

#### *Action of Quinoline on 1 : 2-Dibromohexahydrobenzene.*

Forty-two grams of 1 : 2-dibromohexahydrobenzene and 90 grams of freshly-distilled quinoline were heated in a long-necked distillation flask attached to a condenser. The mixture gradually darkened in colour, and at  $160^\circ$  a reaction began which was marked at  $178^\circ$ . When the reaction had ceased, the temperature was maintained at  $185-190^\circ$  for ten minutes, the thermometer raised out of the liquid,

and the whole heated until all the liquid boiling below  $100^\circ$  had passed over.

A second quantity of 42 grams of dibromohexahydrobenzene was then treated in exactly the same manner.

The combined clear, colourless distillates weighing 22 grams were again distilled from quinoline, the resulting liquid washed with dilute sulphuric acid, dried over calcium chloride, and then repeatedly fractionated from metallic sodium and the portion boiling at  $81.5$ — $82^\circ$  analysed:

0.1152 gave 0.3789  $\text{CO}_2$  and 0.1092  $\text{H}_2\text{O}$ . C = 89.70; H = 10.53.

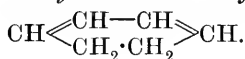
0.1164 „ 0.3824  $\text{CO}_2$  „ 0.1090  $\text{H}_2\text{O}$ . C = 89.60; H = 10.40.

$\text{C}_6\text{H}_8$  requires C = 90.00. H = 10.00 per cent.

$\Delta^{1:3}$ -Dihydrobenzene is a clear, colourless, highly refractive liquid boiling at  $81.5$ — $82^\circ/767$  mm. and possessing a marked odour of leeks.

The author desires to take this opportunity of expressing his most appreciative thanks to Dr. W. H. Perkin, sen., for the interest taken in this work and for kindly determining the following physical data.

*Magnetic Rotation and Refractive Power of  $\Delta^{1:3}$ -Dihydrobenzene,*



The specimen examined, when evaporated on bibulous paper, did not yield any stain, showing that it was free from any polymerised or oxidation products.

The density determinations gave:

$$d_{4^\circ/4^\circ} = 0.8476; d_{15^\circ/15^\circ} = 0.8377; d_{25^\circ/25^\circ} = 0.8296.$$

Magnetic rotation:

$t$ .	Sp. rot.	Mol. rot.
$14.7^\circ$	1.5259	8.093

Refractive power:

$$t = 15.4^\circ; d_{15.4^\circ/4^\circ} = 0.83659.$$

	Index of refraction. $\mu$ .	Sp. refraction. $\frac{\mu - 1}{d}$ .	Mol. refraction. $\frac{\mu - 1}{d} p$ .
$\text{H}_\alpha$ .....	1.46371	0.55429	44.34
$\text{H}_\beta$ .....	1.47672	0.56984	45.59
$\text{H}_\gamma$ .....	1.48493	0.57965	46.37
Dispersion $\text{H}_\alpha - \text{H}_\gamma = 2.03$ .			

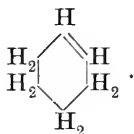
The isomeric dihydrobenzene,  $\text{CH}_2 \begin{smallmatrix} \text{CH:CH} \\ \text{CH:CH} \end{smallmatrix} \text{CH}_2$ , obtained by Miss Fortey (Trans., 1898, 73, 945), had a density of 0.8499 at  $15^\circ/15^\circ$  and the molecular refraction for  $H_a$  was 44.58. It will be seen that both these values are slightly higher than those obtained in the case of the dihydrobenzene investigated above.

Dr. Perkin adds the following remarks:

"The determination of the magnetic rotation of dihydrobenzene is of considerable interest, because it completes the investigation of the series of compounds which commences with hexamethylene and ends with benzene. We are now in a position to follow the changes in physical properties which occur when the saturated hydrocarbon hexamethylene loses two, four, and then six hydrogen atoms with formation of tetrahydrobenzene, dihydrobenzene, and, lastly, benzene itself. The following are the observed values of the substances in question:

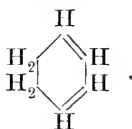
	Mol. rot.	Difference.
Hexamethylene (Trans., 1900, 77, 372) ...	5.664	0.731
Tetrahydrobenzene (Trans., 1898, 73, 942).	6.395	
Dihydrobenzene .....	8.093	1.698
Benzene (Trans., 1896, 69, 1241) .....	11.284	

"The difference in rotation between hexamethylene and tetrahydrobenzene (0.731) is very similar to that which occurs when an open chain hydrocarbon is converted into the corresponding unsaturated hydrocarbon containing two atoms of hydrogen less. Thus, for example, the difference between octane,  $\text{C}_8\text{H}_{18}$ , and octylene,  $\text{C}_8\text{H}_{16}$ , is 0.743. It is therefore evident that tetrahydrobenzene is a simple unsaturated hydrocarbon having the constitution represented by the formula

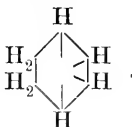


"When, however, tetrahydrobenzene is converted into dihydrobenzene, the increase in value is no less than 1.698, or more than twice that observed in the transformation of hexamethylene into tetrahydrobenzene, whereas in an open-chain compound the increase due to a second double linking is only a little more than that of the first, as in diallyl (Trans., 1895, 67, 262). The former change is obviously of a different character to the latter, and clearly indicates that dihydro-

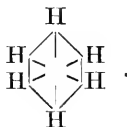
benzene does not contain two ordinary double linkings, and that its constitution is therefore not correctly represented by the formula



“In order to bring out this interesting point, it is suggested that the formula of dihydrobenzene should be written thus :



“When dihydrobenzene is converted into benzene, again with the loss of two atoms of hydrogen, there is a rise in rotation of no less than 3.191, or about four times the difference observed in the conversion of octane into octylene. This great change in physical properties may be indicated by representing benzene by the usual centric formula :



“Whether this is the best method of representation or not is a matter for future investigation to decide, but in any case it is clear that benzene is not derived from hexamethylene by the introduction of three ordinary double linkings, and that it cannot therefore have the constitution represented by Kekulé's formula.

“The value for this latter expression may be approximately calculated by adding to hexamethylene (5.664) three times the difference between octane and octylene ( $3 \times 0.731$ ), and would therefore be 7.857, whereas, as stated above, the value for benzene actually found is 11.284.

“In connection with the question of the relationship between hexamethylene, tetrahydrobenzene, dihydrobenzene, and benzene, it is interesting to observe that, when the values for these substances are plotted out and connected, they form a regular curve, as shown in the following diagram.”

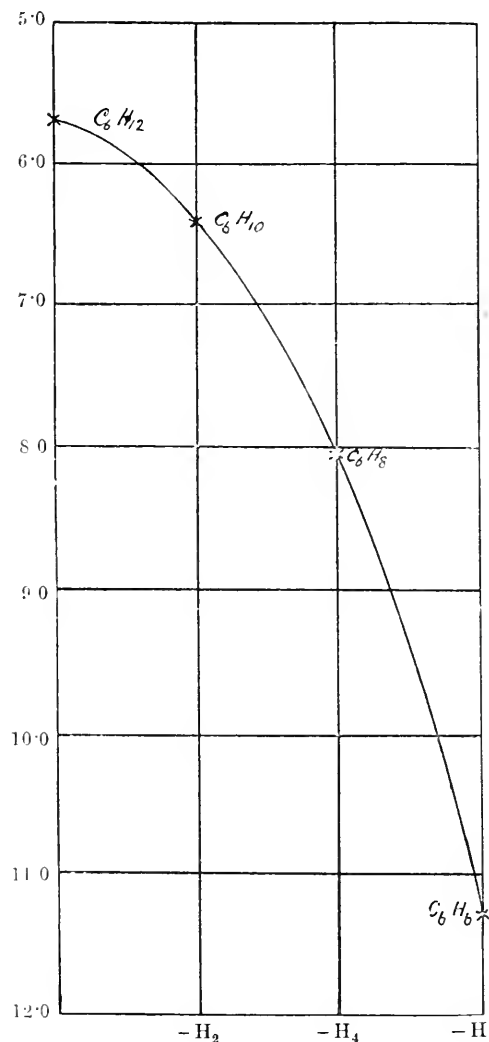
When two drops of  $\Delta^{1:3}$ -dihydrobenzene are dissolved in 2 c.c. of absolute alcohol and concentrated sulphuric acid added drop by drop,

a raspberry-red colour is produced, rapidly turning into a deep blue violet, which remains permanent. The nature of these colour reactions varies greatly with condition of experiment, and in all cases described

in this communication the above-mentioned method of procedure has been adopted.

Even more characteristic is the colour reaction with ordinary concentrated nitric acid (sp. gr. = 1.42), for on adding two or three drops of dihydrobenzene to 5 c.c. of nitric acid, a pink colour is first produced, changing to violet, deep violet-blue, deep purple, reddish-purple, reddish-brown, and finally light brown. The colour changes refer more particularly to the dihydrobenzene, which floats on the surface of the nitric acid, but also to the nitric acid itself.

Dihydrobenzene slowly polymerises, especially if exposed to sunlight, becoming gradually converted into a transparent jelly. A specimen which had been kept in a stoppered bottle for 10 days boiled for the most part at  $81.5$ – $82^\circ$ , but a few drops remained in the distillation flask which



did not evaporate from filter paper, and on further heating decomposed, giving off heavy fumes having an odour somewhat resembling acrolein.

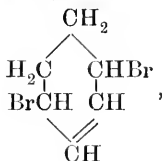
Dihydrobenzene instantly decolorises a chloroform solution of

bromine; the amount of halogen taken up corresponds exactly with the absorption of two atoms of bromine.

1.1522 absorbed 2.3268 Br. Molecular absorption,  $\text{Br} = 161.5$ .

$\text{C}_6\text{H}_8$  requires  $\text{Br}_2 = 160$ .

On evaporating the chloroform used in the above determination, there remained a viscid, slightly coloured liquid, which rapidly deposited crystals (2 grams). These were filtered off and dissolved in light petroleum ( $40\text{--}60^\circ$ ), when on cooling, needles separated, or on slow crystallisation, fern-like aggregates of parallel needles were deposited, melting at  $108\text{--}109^\circ$  and decomposing with evolution of hydrogen bromide at  $170^\circ$ . This substance, 1:4-dibromo- $\Delta^2$ -tetrahydrobenzene,



was proved to be in every respect identical with the dibromodihydrobenzene already described (Trans., 1903, 83, 504). The melting point, which was originally given as  $104.5^\circ$ , is somewhat higher, namely,  $108\text{--}109^\circ$ , and this agrees with the melting point of a substance isolated by Markownikoff (*Annalen*, 1898, 302, 34) by the action of bromine on dihydrobenzene, but not identified.

The action of bromine on dihydrobenzene is a very violent one, and it is best to work with small quantities of the hydrocarbon and to add the bromine very gradually, otherwise during the addition hydrogen bromide is evolved and liquid products formed, from which the dibromide crystallises very slowly.

*Action of Quinoline on 1:4-Dibromo- $\Delta^2$ -tetrahydrobenzene.*

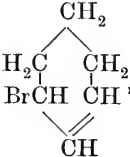
Seven grams of dibromotetrahydrobenzene and 15 grams of quinoline were heated in a distillation flask attached to a condenser, when a reaction took place similar to that described on page 1416. The distillate was free from bromine, and, after washing with dilute sulphuric acid, it was dried over calcium chloride and distilled from metallic sodium. The resulting colourless, highly refractive liquid boiled at  $80\text{--}81^\circ$ , had the characteristic odour of benzene, did not decolorise a chloroform solution of bromine, and on warming with a mixture of concentrated sulphuric and fuming nitric acids was converted into *m*-dinitrobenzene (m. p.  $90^\circ$ ).

*Action of Hydrogen Bromide on  $\Delta^{1:3}$ -Dihydrobenzene.*

Six grams of dihydrobenzene were dissolved in an equal bulk of glacial acetic acid and an excess of a saturated solution of hydrogen bromide in glacial acetic acid added in small quantities at a time. The solution became hot and when left gradually developed a violet coloration. The product was therefore poured into a large excess of water, the heavy oil which separated extracted with ether, the ethereal solution washed with water, then with dilute sodium carbonate solution until no longer acid, finally with water, then dried over calcium chloride, and the ether evaporated. The residual oil, weighing 10 grams, was distilled in a vacuum and the bromine determined.

0.1494 gave 0.1726 AgBr. Br = 49.16

$C_6H_9Br$  requires Br = 49.68 per cent.

1-Bromo- $\Delta^2$ -tetrahydrobenzene, , is a clear, colourless,

highly refractive liquid boiling without any sign of decomposition at  $74^\circ/28$  mm. and possessing a pungent odour somewhat resembling geranium. It is very susceptible to the action of moisture and on exposure to the air rapidly darkens and becomes cloudy; but it can be kept in a dry atmosphere without undergoing decomposition. It would appear to be a very reactive compound, for concentrated ammonia converts it into a substance which gives the carbylamine reaction, and it also reacts with sodium phenoxide to give a viscid liquid boiling at about  $250^\circ$ , but the amount was not sufficient to allow of these reactions being more closely investigated.

On adding a chloroform solution of bromine directly to bromotetrahydrobenzene, the colour of the former slowly disappears, and an attempt was therefore made to determine the bromine absorption. In doing these absorptions, about 1 gram of the substance is dissolved in 20—25 c.c. of chloroform and a 15—20 per cent. solution of bromine in chloroform gradually added, while the whole is cooled in ice-water. As will, however, be seen from the tabulated results, bromotetrahydrobenzene does not behave towards bromine as an ordinary unsaturated substance. The absorption of the bromine takes place extremely slowly and there is no sharp end result, thus making it impossible to draw any definite conclusion from the experiment.

Substance used.	Time.	Bromine absorbed.		Molecular absorption.	
		Found.	Calc.	Found.	Calc.
0.6872	$\frac{1}{2}$ hour	0.2331	0.6829	54.6	160
„	3 hours	0.6164	„	144.4	„
„	6 hours	0.7881	„	184.6	„

*Oxidation of  $\Delta^{1:3}$ -Dihydrobenzene.*

Two grams of dihydrobenzene were added to a mixture of 12 c.c. of concentrated nitric acid (sp. gr. 1.42) and 6 c.c. of water contained in a flask attached to a condenser by means of a ground-glass stopper. On warming on the water-bath, the contents of the flask became pale violet, gradually changing to pure blue; the colour then suddenly disappeared, and a rather violent oxidation set in. After this had subsided, the contents of the flask were heated on the water-bath until the oxidation was complete, filtered from a small quantity of insoluble matter which contained nitrogen, and probably consisted of nitro-aromatic substances, and then evaporated on the water-bath with frequent addition of water until all the nitric acid had been expelled. The product gradually deposited large, needle-shaped crystals which melted at  $100^{\circ}$ , evolved carbon monoxide on heating with strong sulphuric acid, and in neutral solution gave a white precipitate with calcium chloride insoluble in acetic acid, and evidently consisted of oxalic acid. The solid residue obtained on evaporating to complete dryness was heated with excess of acetyl chloride for two hours. On evaporating the solvent, 0.7 gram of a residue remained, which was proved to consist of succinic anhydride by the following data.

On heating with resorcinol and a drop of sulphuric acid, then treating with potassium hydroxide and pouring into water, it gave a very marked fluorescein reaction. It crystallised from absolute alcohol in long, glistening needles melting at  $118-119^{\circ}$ , which, on solution in benzene and treatment with aniline, gave an anilic acid crystallising from water in bunches of flattened needles melting at  $148^{\circ}$ . The corresponding anil, obtained by heating the anilic acid to boiling, crystallised from dilute alcohol in long, slender, glistening needles melting at  $154-155^{\circ}$ .

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ST. THOMAS'S HOSPITAL.



In correspondence with this view, they further found that by conducting Perkin's condensation of *p*-nitrotoluene with alcoholic soda under carefully regulated conditions, the product could be obtained in a crystalline form, which gave on analysis numbers corresponding with a dinitrosostilbene,  $C_{14}H_{10}O_2N_2$ .

In accordance with either of these two views of the constitution of the primary yellow colouring matter, its alkaline reduction product (Mikado or Direct Orange) would have to be regarded as the azo-

stilbenedisulphonic acid,  $\begin{array}{c} \text{CH} \cdot \text{C}_6\text{H}_3(\text{SO}_3\text{H}) \cdot \text{N} \\ || \qquad \qquad \qquad || \\ \text{CH} \cdot \text{C}_6\text{H}_3(\text{SO}_3\text{H}) \cdot \text{N} \end{array}$ . It would, however, be

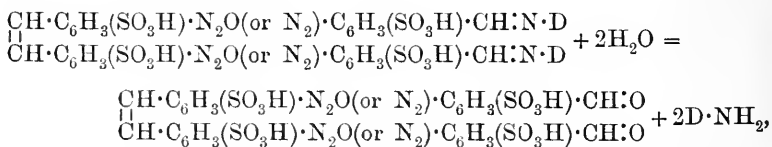
difficult on these lines to assign a formula to the oxidation products (Mikado Golden-yellows).

It is proposed in the following account to collate the results of a series of investigations in this group which I have had in progress for several years, and which, although not yet complete, serve to throw some light on the constitution of these colouring matters. From the outset, it has appeared to me improbable that a substance having the constitution of a simple azoxy- or dinitroso-stilbene should be a dye, no cases being hitherto known in which the introduction of these substituents into hydrocarbon residues produces tinctorial properties.

This work was commenced in 1896, when, in conjunction with A. Wahl, I repeated a portion of the researches of Fischer and Hepp and of Bender. The results obtained led us to believe that these chemists had not worked with chemically pure products, and that the composition of the primary colouring matters may vary considerably according to the conditions employed in the condensation. We further found that the product of the oxidation of the primary colouring matter with chromic acid was not, as asserted by Fischer and Hepp, dinitrostilbenedisulphonic acid, but a greenish-yellow colouring matter apparently identical with the Mikado Golden-yellow of commerce. The true dinitrostilbenedisulphonic acid, which we prepared later (*Ber.*, 1898, 31, 354), is a well-crystallised, colourless compound having no dyeing power and possessing entirely different properties from the above substance.

In the same year, we also discovered a new yellow dye (which was termed "Curcuphenine"), obtained by condensing *p*-nitrotoluenesulphonic acid with dehydrothiotoluidinesulphonic acid in presence of dilute caustic soda (*Eng. Pat.* 12922 of 1896). This colouring matter (manufactured for a time by the Clayton Aniline Co.) possessed great outward similarity to Curcumine, dyed cotton directly with very similar shade, and on alkaline reduction gave colouring matters resembling the Mikado Oranges. All these products differed, however, from those of the Curcumine class in being less soluble in water. On treatment with nitrous acid, they were decomposed

(hydrolysed) into diazotised dehydrothiitoluidinesulphonic acid and a much more soluble yellow or orange dye, which also had the general properties of the stilbene series and dyed the same shade as the original. The latter dyes were found, however, to contain aldehydic groups, the presence of which was demonstrated by the formation of condensation products with hydrazines and by the production of triphenylmethane products with tertiary amines. By following the hydrolysis quantitatively, it was ascertained that it took place somewhat in accordance with the equation :

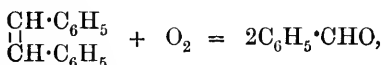


in which D represents the radicle of dehydrothiitoluidinesulphonic acid.

Curcuphenine Yellow and its orange reduction products are therefore imides of stilbene aldehydes in which the dehydrothiitoluidinesulphonic acid simply functions as a primary amine, which, owing to its sparing solubility, combines with the aldehydic groups as they are formed and protects them from further action.

These observations indicated that Curcumine cannot have the simple structure previously assigned to it, since here we have closely allied colouring matters which contain both stilbene and aldehydic groups and must consequently be formed by condensation of at least four molecules of *p*-nitrotoluene. The fact was also demonstrated that under suitable conditions, alkaline condensation of *p*-nitrotoluenesulphonic acid may give rise to direct formation of aldehydic groups, which, by undergoing subsequent condensation, may conceivably play an important part in the stilbene condensation, or cause partial reduction of the colouring matter first formed. These considerations led us to seek for such aldehydic colouring matters amongst the products of the normal condensation of *p*-nitrotoluenesulphonic acid, and we were, in fact, able to prove their presence in these products by means of the phenylhydrazine reaction. This reagent in dilute acetic acid solution produces with such aldehydic colouring matters, whether in bulk or dyed on cotton, a change of colour from yellow to orange-brown. In this manner we demonstrated that commercial Curcumine and Direct Yellows all contain a certain quantity of such aldehydic products, the amount of which decreases as the caustic soda solution employed in their preparation is more concentrated. By boiling *p*-nitrotoluenesulphonic acid with very dilute caustic soda, or better, with sodium carbonate under an inverted condenser for several hours, or

even by heating the sodium salt with distilled water in an iron pipe at 150°, we were able to obtain upwards of 30 per cent. of such aldehydic products (Eng. Pat. 6760 of 1898). These products did not consist alone of stilbene aldehydes, but were a mixture of the latter with aldehydes of the benzene series, apparently azo- or azoxy-benz-aldehydesulphonic acid,  $\text{CHO} \cdot \text{C}_6\text{H}_3(\text{SO}_3\text{H}) \cdot \text{N}_2 \cdot \text{C}_6\text{H}_3(\text{SO}_3\text{H}) \cdot \text{CHO}$ , or the corresponding aldehyde alcohols. We were able to separate these non-dyeing aldehydes from the stilbene aldehydes by their different solubility in salt solution, but did not obtain them in a state sufficiently pure for analysis. As, however, it was found later by ourselves (Eng. Pats. 21825 of 1897; 1431 of 1898; 4045 of 1898) and others that all stilbene derivatives readily give rise to aldehydes by alkaline oxidation:



it still remains undecided whether the above aldehydic compounds are primary products or whether they are formed by the oxidation of the stilbene derivatives first produced.

Starting from the supposition that the formation of a colouring matter from *p*-nitrotoluenesulphonic acid under the influence of alkalis takes place in two stages, in the first of which the methyl group is oxidised by the nitro-group of another molecule, and in the second the product formed undergoes subsequent condensation, I endeavoured in 1887, in conjunction with Wahl, to carry out these supposed stages separately (Eng. Pat. 5357 of 1897; *Ber.*, 1897, 30, 3097; 1898, 31, 1078). By oxidising *p*-nitrotoluenesulphonic acid with sodium hypochlorite in the presence of caustic soda, we succeeded in obtaining, according to the conditions selected, either dinitro-

dibenzylsulphonic acid,  $\begin{array}{c} \text{CH}_2 \cdot \text{C}_6\text{H}_3(\text{SO}_3\text{H}) \cdot \text{NO}_2 \\ | \\ \text{CH}_2 \cdot \text{C}_6\text{H}_3(\text{SO}_3\text{H}) \cdot \text{NO}_2 \end{array}$ , or dinitrostilbene-disulphonic acid,  $\begin{array}{c} \text{CH} \cdot \text{C}_6\text{H}_3(\text{SO}_3\text{H}) \cdot \text{NO}_2 \\ | \\ \text{CH} \cdot \text{C}_6\text{H}_3(\text{SO}_3\text{H}) \cdot \text{NO}_2 \end{array}$ .

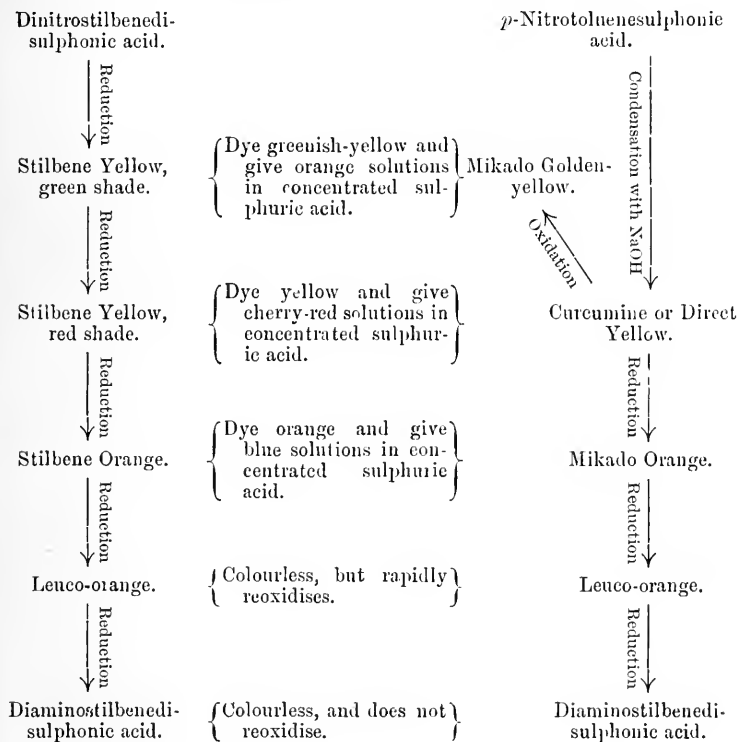
The former was obtained by using hypochlorite equivalent to half of an atom of oxygen and employing a large excess of caustic soda; the latter by using hypochlorite equal to 1 atom of oxygen with less caustic soda and a higher temperature. The dinitrodibenzylsulphonic acid had been previously isolated in an impure state by Bender as a by-product in the formation of Curcumine, and it was also obtained (mixed with some dinitrostilbenedisulphonic acid) by Ris and Simon nearly simultaneously with ourselves. Both acids are beautifully crystallised, colourless products. Although outwardly similar, they differ from each other sharply in the fact that whereas the dibenzyl derivative is not affected by permanganate,

the stilbene derivative is instantly oxidised even in cold dilute aqueous solution to two molecules of *p*-nitrobenzaldehydesulphonic acid,  $C_6H_5(NO_2)(CHO) \cdot SO_3H$ . This reaction is quantitative and forms a convenient method of estimating the acid. The dinitrostilbenedisulphonic acid also differs from the dibenzyl acid in the ease with which it is converted into a carmine-red colouring matter by the action of alkaline reducing agents, as, for instance, alkaline phenylhydrazine or lead clippings and caustic soda (see p. 1430). This forms a ready means of identification by which I have been able to prove its presence amongst the products of the Curcumine condensation. The behaviour of the two acids with caustic alkalis and with reducing agents is very instructive. By boiling dinitrodibenzylsulphonic acid with caustic soda, it behaves in a somewhat similar manner to *p*-nitrotoluenesulphonic acid, a yellow colouring matter being produced together with dinitrostilbenedisulphonic acid. On the other hand, the dinitrostilbenedisulphonic acid gives no such colouring matter when heated alone with caustic soda, but in presence of a small quantity of an oxidisable substance, such as glycerol or glucose, it yields a dye apparently identical with that from the dinitrodibenzyl acid. These colouring matters, which are manufactured by the Clayton Aniline Co. under the name of "Stilbene Yellows," have dyeing properties similar to those of Curcumine, and Direct Yellow, from which they differ, however, in possessing a greener shade and in their freedom from alkali-sensitive and aldehydic by-products (Eng. Pats. 21399 and 21553 of 1897).

In dyeing and other properties, the greenest of these colouring matters closely resembles the Mikado Golden-yellow obtained by oxidation of Curcumine. When submitted to further reduction (for example, with caustic soda and glucose), it gives successively colouring matters which dye cotton yellow, reddish-yellow, yellowish-orange, and reddish-orange. At the same time, the colour of the solution in concentrated sulphuric acid changes from orange to cherry-red, and thence through violet to blue. On carrying this reduction still further, the orange is first decolorised to the leuco-compound and finally reduced completely to diaminostilbene. When the reduction is very slight, the product dyes a shade of yellow closely resembling Direct Yellow or Curcumine, and dissolves in strong sulphuric acid with the same cherry-red colour. It therefore appears probable that the reduction products of dinitrostilbenedisulphonic acid differ from the Curcumine series only in their greater purity and freedom from aldehydic and alkali-sensitive by-products, and, shade for shade, are otherwise chemically identical. The greener tint of the "Stilbene Yellow" as compared with "Curcumine" or "Direct Yellow" indicates a somewhat higher state of oxidation, the difference

being probably explained by the reducing action exerted in the latter case by the aldehydic by-products present.

These relations are expressed by the following scheme :



In addition to the dyes obtained as above, we also found that the two dinitro-acids were capable of forming yellow condensation products with primary amines. The latter colouring matters are, however, of a different type to the "Curcuphenine" colours mentioned earlier, and appear to be mixed azo-(or azoxy-)compounds. That they are not, like Curcuphenine, aldehyde-imides (azomethine compounds) is proved by the fact that they are not hydrolysed by nitrous acid, the product, for instance, from dehydrothiotoluidinesulphonic acid remaining quite unaltered under this treatment. A colouring matter of this type, obtained by condensing dinitrostilbenedisulphonic acid with aniline, is manufactured by Geigy & Co. under the name of "Diphenyl Citronine."

The existence of these dyes of mixed type again indicates a complex structure for the stilbene colours.

When *p*-nitrotoluenesulphonic acid is heated with aqueous caustic

soda, the formation of a crimson-red colour is always first observed, and only on longer heating does this disappear and give place to the orange-yellow colour of the Curcumine itself. This unstable crimson compound therefore marks an intermediate stage in the formation of Curcumine, and the determination of its constitution would probably afford the key to the entire reaction. This crimson compound, the isolation of which is not possible on account of its ready oxidisability in air, has the characteristic property of forming a blue lead salt.

Not only *p*-nitrotoluenesulphonic acid, but also *p*-nitrotoluene itself and a number of its ortho-substituted derivatives give, on treatment with caustic alkalis, deeply coloured intermediate compounds which on further heating are converted into analogues of Curcumine. It has been ascertained by W. S. Stainton and myself that the readiness with which such substituted *p*-nitrotoluenes undergo this change is dependent on the character of the ortho-substituting group. Thus, whilst the sulphonic acid,  $C_6H_3(CH_3)(NO_2)(SO_3H)[1:4:2]$ , only commences to react at about  $60^\circ$ , its phenyl ester,  $C_6H_3(CH_3)(NO_2) \cdot SO_3 \cdot C_6H_5$ , phenylsulphone,  $C_6H_3(CH_3)(NO_2) \cdot SO_2 \cdot C_6H_5$ , and sulphonamide,

$$C_6H_3(CH_3)(NO_2) \cdot SO_2 \cdot NH_2,$$

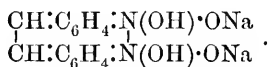
react easily in the cold. Moreover, the intermediate products in the latter cases are blue instead of red.

In studying the action of alkaline hypochlorites on *p*-nitrotoluenesulphonic acid, I had already found, in 1896, that the dinitrostilbenedisulphonic acid did not arise by direct oxidation of the *p*-nitrotoluenesulphonic acid itself, but was formed from the above-mentioned crimson intermediate compound. It was observed, indeed, that the best yields of the stilbene acid were obtained by choosing conditions favourable to the formation of the crimson product and running in sodium hypochlorite just sufficiently fast to decolorise it as it is formed. It was also found, conversely (Eng. Pat. 3393 of 1898), that dinitrostilbenedisulphonic acid was readily converted by alkaline reducing agents into an unstable crimson-red product which in all its reactions closely resembled the above-mentioned substance. An intimate relationship was therefore indicated between the dinitrostilbenedisulphonic acid and the crimson compound, and it seemed likely that their formulæ only differed by two atoms of oxygen.

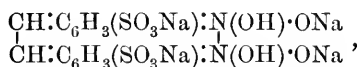
A certain doubt, however, was introduced by the fact that it was never found possible to obtain a larger yield of dinitrostilbenedisulphonic acid than 65 per cent., and this number in particular seemed to suggest the possibility of a trinuclear formula for the crimson compound, and the formation, by oxidation, of a second substance besides dinitrostilbenedisulphonic acid. As will be shown in the following communication, this doubt has now been removed by the preparation of dichlorodinitrostilbene in theoretical yield by oxidation

of the violet-red intermediate product from *o*-chloro-*p*-nitrotoluene. In a similar manner, by oxidation of the blue intermediate product from phenyl *p*-nitrotoluenesulphonate, the diphenyl ester of dinitrostilbenedisulphonic acid is obtained in good yield.

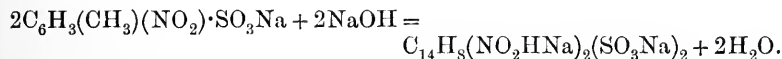
There seems, therefore, every reason for regarding these intermediate compounds as nitrosostilbenes or stilbene nitrolic acids, and since they are only coloured in alkaline solution, it is possible that under these conditions they have a quinonoid structure of the type :



The crimson-red compound from *p*-nitrotoluenesulphonic acid would accordingly have the constitution :



and its formation would be represented by the equation :



In the subsequent condensation of these nitroso-compounds to colouring-matters of the Curcumine class, it may be supposed that two molecules take part.

In conclusion, I desire to acknowledge my indebtedness for the valuable assistance rendered me by my former colleagues, Mr. A. Wahl, Dr. A. Mayenberg, Mr. R. Levy, and Mr. E. Wray, and to express my thanks to the Clayton Aniline Co., in whose laboratory the earlier part of the above work was conducted.

THE UNIVERSITY,  
LEEDS.

# CXIIV.—*The Colouring Matters of the Stilbene Group.* II.

By ARTHUR GEORGE GREEN, FRED MARSDEN, AND FRED SCHOLEFIELD.

THE production of coloured stilbene derivatives which takes place when *p*-nitrotoluene, or almost any one of its ortho-substituted derivatives, is heated with caustic alkalis is invariably preceded by the formation of an unstable, highly coloured intermediate substance. It has been observed by Green and Stainton that the facility with which these intermediate compounds are formed, and also their shade, depends on the character of the ortho-substituent. Thus, whilst the ortho-sulphonic acid reacts at about 60°, producing a crimson-red compound, the sulphonamide, phenyl sulphonate, and phenyl sulphone all react in the cold, producing blue compounds, and the ortho-chloro-derivative reacts between 20° and 30° with formation of a violet-red compound.

The object of the present research was to throw further light on the constitution of these coloured intermediate products in the hope of thus obtaining the key to the mechanism of the stilbene condensation and the structure of the stilbene colouring matters. We selected for examination the chloro-derivative,  $C_6H_3(CH_3)(NO_2)Cl[1:4:2]$ , and the phenyl sulphonate,  $C_6H_3(CH_3)(NO_2)(SO_3 \cdot C_6H_5)[1:4:2]$ , partly on account of their ready reactivity and partly in the expectation of obtaining well crystallised definite compounds capable of purification and analysis. We also had the intention, in the case of the phenyl sulphonate, to convert the end-products by saponification into soluble colouring matters, and thus compare them with the known dyes of the stilbene series.

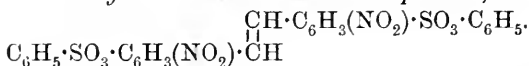
## *Action of Caustic Alkalis on Phenyl p-Nitrotoluenesulphonate.*

The phenyl sulphonate was prepared by converting sodium *p*-nitrotoluenesulphonate into the sulphonic chloride by the action of chlorosulphonic acid and treating the sulphonic chloride with sodium phenoxide.

One hundred grams of the dry sodium sulphonate were added in small portions to 220 c.c. of chlorosulphonic acid, keeping the temperature below 45°. After an hour or two, the mixture was poured on to ice and the precipitated chloride collected and dried in the air. It was purified by dissolving in benzene, filtering from dirt, and allowing the benzene to evaporate. The chloride so ob-

tained was dissolved in an excess of phenol, and caustic soda was slowly added, taking care that the mixture did not become alkaline. The whole was then poured into water and the precipitated phenyl sulphonate purified by crystallisation from alcohol. It is a well-crystallised colourless compound, which melts at  $64^{\circ}$  and is not easily saponified. On the addition of aqueous or alcoholic caustic soda or potash to its cold alcoholic solution, the latter assumes momentarily an orange-yellow colour, but within a few seconds this is replaced by a greenish-blue, which quickly becomes intense pure blue. If the experiment is conducted in an atmosphere of hydrogen and kept cold, the blue colour persists for some time, slowly becoming more violet, and finally changing to a slaty-grey. If the blue solution is neutralised by acetic acid or by passing in carbon dioxide, a yellow solution is obtained, in which is suspended an orange-yellow, amorphous precipitate. Many attempts were made to obtain this compound in a condition suitable for analysis, but by reason of its unstable and oxidisable character this could not be accomplished. Even in the process of acidification, it appeared to undergo decomposition, for the blue colour was not regenerated in its original purity on again rendering alkaline. The attempt at isolation was therefore abandoned, and we endeavoured to determine its constitution indirectly by examining its oxidation products. For this purpose, we employed as oxidising agents either sodium hypochlorite or air.

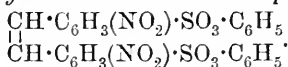
*Oxidation of the Blue Intermediate Compound by Sodium Hypochlorite.*—Ten grams of the phenyl sulphonate were dissolved in 500 c.c. of alcohol and 60 c.c. of 50 per cent. aqueous caustic potash were added to the quite cold solution. An aqueous solution of sodium hypochlorite containing 6.9 per cent. of active chlorine was run in at the same rate as that at which the formation of the blue colour took place, so that the colour was destroyed immediately it was formed. The hypochlorite was added until no further formation of colour occurred. The quantity of hypochlorite required varied considerably with the strength of the solution and the quantity of caustic potash employed; it was usually in considerable excess of the theoretical amount, as a portion was destroyed in oxidising some of the alcohol. The product of the reaction separated out as a colourless, crystalline powder. This was collected, washed successively with hot alcohol and water, and dried. The yield varied between 50 and 70 per cent. It melted indefinitely at  $170$ – $190^{\circ}$  and was found to consist of two isomerides, namely, the *trans*- and *cis*-modifications of phenyl dinitrostilbenedisulphonate. The filtrate contained as a by-product the dinitrostilbenedisulphonic acid of Green and Wahl, evidently formed by saponification of the phenyl ester. Dinitrodibenzyl compounds are apparently not produced.

*Phenyl trans-Dinitrostilbenedisulphonate,*

The mixture of isomerides obtained as above was found to be best separated by the following method:—The product was dissolved in a small quantity of boiling chloroform and about half the volume of hot ethyl acetate was added. The crystalline precipitate was filtered off from the hot solution at the pump and recrystallised from chloroform. It separated in slightly yellow, rhombic prisms, sometimes having pyramidal truncations.

It melted sharply at 192—192·5°, was sparingly soluble in alcohol and ethyl acetate, more readily in acetone and benzene, easily in glacial acetic acid and hot chloroform.

	Found.		$\text{C}_{14}\text{H}_8(\text{NO}_2)_2(\text{SO}_3 \cdot \text{C}_6\text{H}_5)_2$ requires.
	I.	II.	
Carbon.....	54·43	53·61	53·60
Hydrogen .....	4·12	3·40	3·09
Nitrogen .....	4·91	—	4·81
Sulphur .....	12·02	11·3	11·0

*Phenyl cis-Dinitrostilbenedisulphonate,*

The hot chloroform and ethyl acetate filtrate obtained as above, after collecting the *trans*-isomeride, deposited on cooling the *cis*-isomeride in small crystals which, on recrystallisation from amyl alcohol, formed elongated yellow lamellæ.

It melted at 172° and, in most solvents, was more soluble than the *trans*-isomeride.

	Found.	$\text{C}_{14}\text{H}_8(\text{NO}_2)_2(\text{SO}_3 \cdot \text{C}_6\text{H}_5)_2$ requires.
Carbon .....	53·90	53·60
Hydrogen.....	3·49	3·09
Nitrogen .....	5·04	4·81
Sulphur .....	12·0	11·0

For further characterisation of these compounds as phenyl esters of dinitrostilbenedisulphonic acid, this acid was submitted to direct phenylation. For this purpose we employed the commercial sodium salt which was kindly supplied to us by the Clayton Aniline Co. This was converted into the sulphonic chloride by dissolving in about eight times its weight of chlorosulphonic acid, heating at 90—95° for a few minutes, and after cooling pouring carefully on to ice. The yellowish-white, granular precipitate of the chloride was collected at the

pump, washed with water, and dried in the air. To convert it into the phenyl ester, 6 grams were dissolved in 40 grams of phenol with the addition of 3 c.c. of pyridine. The solution was warmed slightly, and 3 c.c. of 50 per cent. aqueous caustic potash were slowly added, keeping the temperature at about 60° for twenty minutes. The mixture was then poured into dilute caustic soda solution, and the precipitated ester collected, washed, and dried. It was found to be a mixture of two substances, which were separated by recrystallisation from solvents. By their melting points and other properties they were identified as the two isomeric phenyl esters described above. By both methods of preparation, the *cis*-compound is formed in smaller quantity than its *trans*-isomeride.

The above experiment also brings to light the interesting fact that Green and Wahl's dinitrostilbenedisulphonic acid (*Ber.*, 1897, 30, 3097) is in reality a mixture of two stereoisomerides, and since it is formed by oxidation of the crimson intermediate product formed in the preparation of Curcumine, it is probable that this intermediate product and the stilbene dyes to which it gives rise are also mixtures of *cis*- and *trans*-isomerides. It is hoped later to study the influence on the colour which this isomerism may be expected to produce.

*Oxidation of the Blue Intermediate Compound by Air.*—The blue compound formed by the action of caustic alkalis on a cold alcoholic solution of phenyl *p*-nitrotoluenesulphonate is very rapidly decolorised by air, and we have carried out a series of oxidations using air in place of hypochlorite. The product obtained was found to consist of the same two phenyl dinitrostilbenedisulphonates, but the yield was far less satisfactory. Thus 1 gram of the phenyl ester was dissolved in 75 c.c. of alcohol, the solution cooled with ice, and 5 c.c. of 50 per cent. caustic potash added, while a stream of air was passed through until the development of colour had ceased. The product which separated was collected and washed successively with hot alcohol and water. Only 0.2 gram of the product was obtained, the low yield being due to the large amount of saponification which simultaneously occurs, for the filtrate was found to contain a considerable quantity of dinitrostilbenedisulphonic acid. The ease with which this saponification takes place contrasted with the stability of the phenyl esters under ordinary conditions is very remarkable, and led us to attribute its occurrence to the formation of hydrogen peroxide during the oxidation. We were able in fact to prove the presence of this substance by the addition of lead acetate to the reacting mixture, when lead peroxide was formed and could be filtered off and identified by the liberation of chlorine, which occurred on dissolving the precipitate in hydrochloric acid. The hydrolytic action of sodium peroxide has been observed previously in a few cases.

*Action of Caustic Alkalis and Oxidising Agents on o-Chloro  
p-nitrotoluene.*

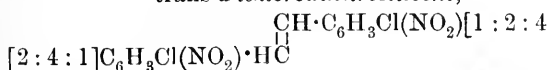
The *o*-chloro-*p*-nitrotoluene was prepared from *p*-nitro-*o*-toluidine (1 : 2 : 4) by Sandmeyer's reaction and purified by distillation with steam. It separates from hot alcohol in long, colourless prisms which melt at 65°. On adding to its alcoholic solution, warmed to 25° or 30°, a concentrated aqueous or alcoholic solution of caustic potash or soda, a deep reddish-purple solution of the intermediate product is obtained. No attempt was made to isolate this, but it was at once submitted to oxidation. Both sodium hypochlorite and air were employed as oxidising agents, the same products being obtained in either case. In employing sodium hypochlorite, the following proportions were found to give good results:—

Ten grams of *o*-chloro-*p*-nitrotoluene were dissolved in 200 c.c. of alcohol; 100 c.c. of saturated alcoholic potash were added, followed immediately by an aqueous solution of sodium hypochlorite, containing about 7 per cent. of active chlorine, which was slowly run into the slightly warmed solution at just sufficient speed to decolorise the purple colour as rapidly as it formed. When the development of colour ceased, the addition of hypochlorite was stopped, and the crystalline precipitate formed was filtered off, washed with alcohol, and dried.

When air was employed as the oxidising agent, the solution was placed in a flask, the caustic alkali added, and a rapid current of air drawn through the solution by means of the vacuum pump, the mixture being heated at 45–50° by immersion in hot water. When no further production of purple colour took place on stopping the air current, the time usually required being about twenty minutes, the light, crystalline precipitate was collected, washed with water, and dried. The yield was over 90 per cent. of the weight of the chloro-nitrotoluene.

The product was found to be almost insoluble in alcohol, acetone, ether or benzene, slightly soluble in chloroform, amyl alcohol or solvent naphtha, more soluble in nitrobenzene, phenol or aniline. The substance was evidently a mixture, since its melting point ranged from 200° to 300°. After some difficulty, we finally succeeded in effecting a separation by dissolving in boiling phenol, allowing to cool to about 80°, and filtering off the portion which crystallised out. On repeating this treatment and recrystallising finally from nitrobenzene, the least soluble constituent was obtained in a pure state. It proved to be

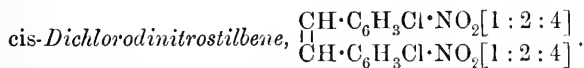
*trans-Dichlorodinitrostilbene,*



This compound, which forms much the greater portion of the oxidation product, crystallises in orange-yellow needles melting at 302°. It is nearly insoluble in all solvents with exception of hot nitrobenzene and phenol, in which it is moderately soluble.

	Found.	$C_{14}H_8Cl_2(NO_2)$ requires.
Carbon .....	49·54	49·54
Hydrogen.....	2·50	2·36
Nitrogen .....	8·37	8·26
Chlorine .....	21·07	20·94

The substance is readily attacked by a cold acetone solution of potassium permanganate when *o*-chloro-*p*-nitrobenzoic acid (m. p. 137°) was obtained and identified, together with a small amount of an aldehyde. There can therefore be no doubt that the substance has the constitution assigned to it above. The dichlorodinitrostilbene obtained by Witt (*Ber.*, 1892, 25, 77) by the action of alcoholic potash on *o*-chloro-*p*-nitrobenzyl bromide and found to melt at 294° is probably a mixture of the above with a small quantity of the *cis*-isomeride.



This was obtained from the phenolic filtrate after the *trans*-isomeride had crystallised out. The filtrate was neutralised with caustic soda and the pale yellow precipitate filtered off and washed with hot water. The precipitate was boiled with a large amount of alcohol, in which the *cis*-isomeride is somewhat soluble and from which it crystallises out on cooling. Finally, it was obtained pure by recrystallisation from glacial acetic acid or chloroform; it forms small, pale yellow prisms (m. p. 172—173°). It is much more soluble in most solvents than the *trans*-isomeride.

	Found.	$C_{14}H_8Cl_2(NO_2)_2$ requires.
Carbon .....	49·52	49·54
Hydrogen.....	2·73	2·36
Nitrogen .....	8·27	8·26
Chlorine .....	21·09	20·94

#### *Reconversion of Dinitrostilbene Derivatives into the Coloured Intermediate Compounds.*

It was observed by Green and Wahl that the dinitrostilbenedisulphonic acid was readily converted by alkaline reducing agents into a

crimson-red compound very similar in appearance and properties to that formed directly from *p*-nitrotoluenesulphonic acid by the action of caustic soda. We have now ascertained that this reaction is a general one and that all derivatives of dinitrostilbene are reconverted by alkaline reducing agents into the coloured compounds from which they are formed by oxidation. This is also the case with both the *trans*- and *cis*-isomerides. Thus the two phenyl dinitrostilbenedisulphonates above described give intense bright blue colorations, whilst the two dichlorodinitrostilbenes give reddish-purple compounds of exactly the same shade as that obtained by the action of alcoholic potash on the corresponding *p*-nitrotoluene derivatives. Moreover, if before adding the reducing agent the phenyl esters are saponified, the above-mentioned crimson-red colour is obtained instead of blue, clearly showing that the blue compound is the phenyl ester of the red substance. The most convenient method of performing these reactions is to dissolve the stilbene derivative in a little hot chloroform or nitrobenzene, dilute freely with cold alcohol, add some alcoholic potash, and then a few drops of an alcoholic solution of phenylhydrazine, when the colour at once appears. The close relationship which is here proved to exist between these intermediate compounds and the dinitrostilbene derivatives, the latter differing from the former only by containing two additional atoms of oxygen, appears to indicate that these coloured intermediate compounds have the formula of a nitroso-stilbene or nitrolic acid.

The investigation will be continued.

THE CLOTHWORKER'S RESEARCH LABORATORY,  
UNIVERSITY OF LEEDS.

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CXLV.—*Researches on Chromorganic Acids: the Behaviour of Chromic Hydroxide towards Oxalic Acid and certain other Organic Acids.*

By EMIL ALPHONSE WERNER.

*Introductory.*

MANY years ago (Trans., 1886, 49, 383; 1887, 51, 404 and 602), I showed that Gregory's blue salt,  $K_6Cr_2(C_2O_4)_6 \cdot 6H_2O$ , and Croft's red salt,  $K_2Cr_2(C_2O_4)_4 \cdot 10H_2O$ , are not ordinary double salts as was then supposed, but are respectively derivatives of the following chrom-oxalic acids:  $H_6Cr_2(C_2O_4)_6$  and  $H_4Cr_2(C_2O_4)_4(OH)_2$ . Croft's compound was shown to be an acid salt, the composition of which is correctly

represented by the formula  $K_2H_2Cr_2(C_2O_4)_4(OH)_2 \cdot 8H_2O$ , and from which, by addition of alkali, normal green salts can be obtained of the type  $K_4Cr_2(C_2O_4)_4(OH)_2$ .

Since then other chemists, notably Rosenheim (*Zeit. anorg. Chem.*, 1896, 11, 175), Rosenheim and Cohn (*Zeit. anorg. Chem.*, 1901, 28, 337), and more recently Jorissen and Reicher (*Zeit. Farb. Text. Chem.*, 1903, 2, 431), have contributed to the chemistry of these compounds, and have confirmed much of my work.

So far no chromoxalic acid has been obtained and recognised in the solid state, our knowledge being limited to the existence of aqueous, alcoholic, or ethereal solutions, which on neutralisation can afford solid derivatives.

The only known solid compound containing the oxalic group and chromic chromium alone is the substance which is now extensively used as a mordant in dyeing, and under the name of "chromium oxalate" or "chromic oxalate," is commonly regarded as a salt. The commercial article is variable in its composition, and contains an excess either of insoluble chromic hydroxide or of oxalic acid.

I have, from time to time during the last few years, examined the behaviour of chromic hydroxide towards oxalic acid and a number of organic acids, and I now desire to lay my results before the Society, more particularly in view of the work on chromium oxalate published by Wyruboff (*Bull. Soc. franç. Min.*, 1901, 24, 86) and by Rosenheim (*loc. cit.*), whose results differ in many essential points from my own.

#### *Interaction of Chromic Hydroxide and Oxalic Acid.*

When recently precipitated\* and thoroughly well-washed chromic hydroxide is gradually added to a hot aqueous solution of oxalic acid, the hydroxide commences to dissolve at once, and continues to do so until a solution is obtained containing chromium and oxalic acid in the ratio  $Cr_2(C_2O_4)_3$ . When this stage is reached, the chromic hydroxide ceases to dissolve any further.

The clear filtrate has a deep purplish-red colour and a strongly acid reaction; it becomes deep green on the addition of alkali. The presence of the oxalic radicle is not revealed by the usual precipitation tests, and chromic hydroxide is not precipitated by the addition of excess of alkali in the cold. When the original solution is evaporated on the water-bath, it leaves an amorphous, friable residue which by transmitted light has a deep sap-green colour, whilst by reflected light it appears almost jet black. A superficial examination of the sub-

\* Ammonia was always used to prepare the hydroxide, as the substance, when precipitated by sodium or potassium hydroxide, invariably retains alkali in spite of repeated washing.

stance would suggest a crystalline structure, but all the attempts which I have made to obtain a definite crystalline compound from this solution have been so far unsuccessful.

Wyrouboff, in addition to an amorphous chromium oxalate to which he gives no formula, describes an oxalate,  $\text{Cr}_2(\text{C}_2\text{O}_4)_3 \cdot 25\text{H}_2\text{O}$ , forming violet crystals, a hydrate with  $13\text{H}_2\text{O}$  forming grey needles, and also two crystalline hydrates with  $4\text{H}_2\text{O}$  and  $1\text{H}_2\text{O}$  respectively. Rosenheim and Cohn state that the hydrate with  $13\text{H}_2\text{O}$  contains  $16\text{H}_2\text{O}$ , six molecules of which are water of constitution. These crystalline substances were obtained by the addition of an alkali oxalate to chromium solutions. Without going into quite unnecessary detail, I may briefly state that I have not been able to obtain evidence of the existence of any definite crystalline hydrate of chromium oxalate, and am therefore inclined to doubt the existence of such compounds. The results which I shall now describe have been obtained with the amorphous residue from the "chromium oxalate" solution, the preparation of which I have just explained, as experience has shown this to be the most reliable method for obtaining a product capable of affording satisfactory results, provided the following precautions are observed. Before analysing the residue from this solution, it is absolutely necessary to dry the finely-powdered material thoroughly by heating for several hours at  $100^\circ$ , otherwise the percentage of chromium in the apparently dry product may vary from 20—25 per cent. The substance is exceedingly deliquescent; a portion exposed to a moist atmosphere became syrupy after two days, and was more than doubled in weight, while at the end of five weeks it had absorbed over five times its weight of water; this is very different from Wyrouboff's compound with  $25\text{H}_2\text{O}$ , which he states gradually loses  $12\text{H}_2\text{O}$  on continued exposure to the air.

I shall now state, as briefly as possible, the composition and general properties of the different compounds examined, the analytical data and experimental details of the analyses are given later on.

The chromium oxalate, carefully dried at  $100^\circ$ , still contains a considerable proportion of water of constitution, which is only completely expelled at  $210$ — $215^\circ$ ; above this temperature, the oxalic group commences to decompose. The proportion of water corresponds with the ratio  $\text{Cr}_2(\text{C}_2\text{O}_4)_3 \cdot 4\frac{1}{2}\text{H}_2\text{O}$ , from which I conclude that the composition of the compound is best represented by the formula  $\text{Cr}_4(\text{C}_2\text{O}_4)_6 \cdot 9\text{H}_2\text{O}$ .

The substance is extremely soluble in water, the dissolution being slow at first; it also dissolves slowly in alcohol, the addition of ether precipitating the compound from this solution.

Rosenheim appears to have obtained a compound soluble in ether, while Wyrouboff's crystalline oxalates are stated to be insoluble even in water.

The strongly acid reaction of this compound in solution does not appear to have attracted the attention of other investigators; when ammonia or potassium hydroxide is added to the solution, the colour gradually changes from purplish-red to deep green, and the addition of alkali in the ratio of  $2\frac{1}{2}$  molecules to  $\text{Cr}_2$  is required before the liquid assumes a faintly alkaline reaction. The addition of alcohol at this stage precipitates in each case a dark green, amorphous compound, which, after washing thoroughly with alcohol and drying at  $100^\circ$ , is readily soluble in water, affording a perfectly neutral solution. The ammonium derivative is most easily prepared by adding a slight excess of ammonia to the original chromoxalate solution, evaporating to dryness, and heating the residue for a short time at  $100^\circ$ ; this substance has the composition  $(\text{NH}_3)_5\text{Cr}_4(\text{C}_2\text{O}_4)_6 \cdot 7\text{H}_2\text{O}$ ; the existence and properties of this compound at once suggest that five atoms of acidic hydrogen are present in the molecule of chromium oxalate, the formula of which may therefore be written  $\text{H}_5\text{Cr}_4(\text{C}_2\text{O}_4)_6(\text{OH})_5 \cdot 4\text{H}_2\text{O}$ , the ammonium salt dried at  $100^\circ$  being  $(\text{NH}_4)_5\text{Cr}_4(\text{C}_2\text{O}_4)_6(\text{OH})_5 \cdot 2\text{H}_2\text{O}$ .

I have not been able to obtain a corresponding compound containing five atoms of potassium, whilst the pentabasic character towards ammonium appears clear; the potassium derivative, prepared as already described and dried at  $100^\circ$ , has the composition  $\text{K}_4\text{Cr}_4(\text{C}_2\text{O}_4)_6(\text{OH})_4$ . That this is a definite compound is shown by the fact that it dissolves in water, giving a neutral solution; chromic hydroxide is not precipitated when the solution is boiled for some time, and calcium chloride does not give a precipitate of calcium oxalate. When ignited, the compound leaves a residue of  $(2\text{K}_2\text{CrO}_4, \text{Cr}_2\text{O}_3)$  in accordance with the equation:



When an excess of potassium hydroxide is added to the chromoxalic solution, a portion of the oxalic group tends to be eliminated, and ill-defined compounds are precipitated by alcohol. With ammonia in large excess, there is a similar tendency, but a definite compound appears to be always produced.

If the chromoxalic acid in fine powder is directly dissolved in a strong solution of ammonia (the solution of sp. gr. 0.880 diluted with an equal volume of water), the liquid, which at first is dark green and exhibits dichroism, gradually assumes a deep purplish-red colour; alcohol precipitates the new derivative in the form of a dark purplish-red, microcrystalline powder. This substance, after drying by gentle warming to expel all traces of alcohol and free ammonia, gives analytical results suggesting the formula  $(\text{NH}_4)_5\text{Cr}_4(\text{C}_2\text{O}_4)_5 \cdot 5\text{NH}_3 \cdot 14\text{H}_2\text{O}$ .

This compound differs from those already described; it is very unstable, the solution readily gives off ammonia on boiling, and calcium chloride precipitates some calcium oxalate. When the

chromoxalic acid is treated with an excess of sodium hydroxide, a green compound is obtained in which the ratio of Na to Cr is either  $\text{Na}_8\text{Cr}_4$  or  $\text{Na}_{10}\text{Cr}_4$ , the chromium atoms and oxalic groups being always in the ratio of four to five.

Aniline is readily dissolved by the chromoxalic solution and affords derivatives crystallising in well-defined, large, deep purplish-blue prisms; the composition of these products varies with the proportion of aniline used, and their investigation is still in progress. It is hoped that a careful examination of these compounds may help to throw further light on the exact nature of the so-called chromium oxalate.

It is evident, however, from the results of the work recorded in the present paper, that when chromic hydroxide is dissolved by oxalic acid, the product cannot be considered as an ordinary saline compound, but is a true chromoxalic acid, which in solution behaves in accordance with the presence of distinct ions of hydrogen and "chromoxal," the chromium atoms and oxalic groups acting in union as a negative ion. When the chromoxalic solution is boiled with normal potassium oxalate, as might be expected, the red potassium chromoxalate,  $\text{K}_2\text{Cr}_2(\text{C}_2\text{O}_4)_4 \cdot 10\text{H}_2\text{O}$ , is gradually formed, as Rosenheim has already shown, but at the same time a salt forming small, dark blue acicular crystals is produced, the analysis of which, although not yet completed, indicates that the chromium atoms and oxalic groups are in the ratio expressed by the formula  $\text{Cr}_2(\text{C}_2\text{O}_4)_3$ . The production of two distinct salts in this experiment is in favour of the double formula  $\text{Cr}_4(\text{C}_2\text{O}_4)_6$  adopted in this paper.

### *Analytical Data.*

#### *Analyses of the Chromoxalic Compound or "Chromium Oxalate."*

The results appended were obtained with different portions of material which had ceased to lose weight after heating for several hours at  $100^\circ$ .

		Found.			$\text{Cr}_4(\text{C}_2\text{O}_4)_6 \cdot 9\text{H}_2\text{O}$
	I.	II.	III.		requires.
Cr.....	23.47	23.36	23.21		23.16
$\text{C}_2\text{O}_4$ .....	58.29	58.43	58.62		58.79
$\text{H}_2\text{O}$ .....	17.78	17.98	18.09		18.04

Careful attention was given to the estimation of the water, which was collected and weighed, as a mere determination of loss in weight is not trustworthy, as portion of the oxalic group is liable to decompose at the high temperature necessary to expel all the water.

The following experiment is given as an example. 1.0265 grams heated in a slow current of dry air for four hours gave after :

1	hour at 120—130°;	0.098	gram	H <sub>2</sub> O = 9.54	per cent.
1	„ 150—160°;	0.05	„	H <sub>2</sub> O = 4.87	„
1	„ 160—190°;	0.008	„	H <sub>2</sub> O = 0.78	„
1	„ 210°	; 0.0265	„	H <sub>2</sub> O = 2.59	„

amounting in all to 17.78 per cent. of water, and there was only a very slight decomposition of the C<sub>2</sub>O<sub>4</sub> group. It is necessary to increase the decomposition in order to secure the expulsion of the last traces of water.

	Found.	(NH <sub>4</sub> ) <sub>5</sub> Cr <sub>4</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>6</sub> (OH) <sub>5</sub> , 2H <sub>2</sub> O requires.
NH <sub>3</sub> .....	9.25	8.97
Cr .....	22.09	21.96
C <sub>2</sub> O <sub>4</sub> .....	55.74	55.75
H <sub>2</sub> O .....	13.39	13.30

This compound can be heated up to 200° without appreciable loss of ammonia; the first 2 molecules of water are evolved at 140°.

	Found.	K <sub>4</sub> Cr <sub>4</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>6</sub> (OH) <sub>4</sub> requires.
K .....	16.40	16.25
Cr .....	21.82	21.66
C <sub>2</sub> O <sub>4</sub> .....	52.79	55.00
H <sub>2</sub> O .....	(not determined)	

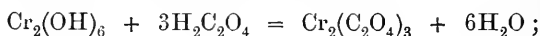
I have not been able to obtain a product affording a higher percentage of the oxalic group; the above corresponds with the formula Cr<sub>4</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>5.74</sub>; as I have already mentioned, there is a great tendency for a portion of the oxalic group to be eliminated by the action of even sufficient alkali to produce neutralisation or faint alkalinity.

	Found.	(NH <sub>4</sub> ) <sub>5</sub> Cr <sub>4</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>5</sub> , 5NH <sub>3</sub> , 14H <sub>2</sub> O requires.
NH <sub>3</sub> .....	15.74	16.38
Cr .....	19.25	18.90
C <sub>2</sub> O <sub>4</sub> .....	40.74	40.87
H <sub>2</sub> O (diff.) .....	23.33	22.94

The difficulty of drying this substance without loss of a trace of ammonia accounts for the rather low result; the determinations of chromium and oxalate in several different specimens have never given a higher ratio than the above, and some ammonium oxalate is always produced as a by-product in the preparation.

*Behaviour of Chromic Hydroxide towards Other Organic Acids.*

The dissolution of chromic hydroxide in a hot solution of oxalic acid takes place very readily, and rapidly reaches the proportion required by theory, according to the equation :



the nature of the solution and the properties of the compound formed have just been described.

With other organic acids, however, the chromic hydroxide shows a very marked difference in behaviour, as, for instance, with the three related compounds, oxalic, malonic, and succinic acids.

In each case, 2.06 grams of recently precipitated and well-washed chromic hydroxide were gradually added to the boiling solution of the acid and the mixture kept boiling for 1 hour, water being added from time to time to replace that lost by evaporation. The proportions of the hydroxide dissolved were as follows: oxalic acid, 100, malonic acid, 49.70, and succinic acid, 0.64.

Whilst, in the case of malonic acid, the proportion of hydroxide dissolved increases slowly with long-continued boiling, this makes no difference with succinic acid, and both in the foregoing and also in all subsequent experiments there was no evidence whatever of the formation of any insoluble basic chromium salts.

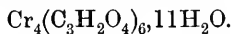
The behaviour of the hydroxide with succinic acid where the interaction is practically nil, even in presence of excess of acid, is somewhat unexpected.

Experiments with glycollic, lactic, malic, tartaric, citric, and tricarballic acids under similar conditions have shown that relatively small proportions of chromic hydroxide are dissolved by these acids, varying from 12 per cent. in the case of malic to 27 per cent. in the case of lactic acid. The chromium solutions produced have in all cases the general characters of the chromoxalic solution, indicating that true chromorganic acids, and not saline compounds, are formed.

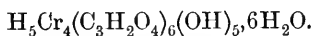
*Chromic Hydroxide and Malonic Acid.*

When chromic hydroxide is dissolved to saturation in a solution of malonic acid, a deep purplish-red liquid is produced, which on evaporation leaves an amorphous, dark green, friable residue containing some uncombined malonic acid. In order to obtain a pure product, the residue is extracted with boiling alcohol, which removes the excess of acid, at the same time dissolving some of the chromium compound; the residue from this treatment is again dissolved in water. The

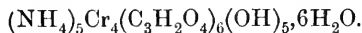
solution, which has a strongly acid reaction, affords on evaporation a greenish-black residue ; this product, when thoroughly dried at 100°, gives analytical results corresponding with the formula



Cr = 20·49 and 20·41,  $\text{H}_2\text{O}$  = 19·4, the calculated percentages being Cr = 20·43 and  $\text{H}_2\text{O}$  = 19·44. The water is only completely expelled at 190°, without any decomposition of the malonic group, six molecules of water being eliminated at 150—160°. This compound is exactly analogous to the chromoxalic derivative, its behaviour towards alkalis indicating a constitution corresponding with a chromomalonic acid of the type :



Thus, when treated with a solution of ammonia in a manner similar to the chromoxalic acid (see p. 1441), a derivative is obtained having the composition



The analytical data gave Cr = 18·55 and 18·78,  $\text{NH}_3$  = 7·58, the calculated percentages being Cr = 18·85 and  $\text{NH}_3$  = 7·70. The above formula requires 17·95 per cent. of water, the highest result was 15·90 per cent., this being obtained by heating to about 160°, at which temperature incipient decomposition takes place.

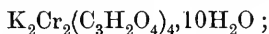
This compound, which affords a perfectly neutral solution in water, is insoluble in alcohol.

A potassium derivative having properties analogous to those of the chromoxalic compound was obtained, but it was not analysed.

A chromomalonate corresponding with Croft's red chromoxalate is obtained by boiling the chromomalonic solution with two molecular proportions of potassium malonate, in accordance with the equation :



This compound separates from its solution in dark purplish-red, rhombic prisms resembling Croft's salt, and has the composition :



it furnishes the following analytical data: Cr = 13·65, K = 10·21,  $\text{H}_2\text{O}$  = 23·01 per cent., the calculated values being Cr = 13·50, K = 10·13,  $\text{H}_2\text{O}$  = 23·37.

At 160—170°, the salt loses  $8\text{H}_2\text{O}$  and becomes dark green ; the last traces of  $\text{H}_2\text{O}$  can only be expelled at temperatures above 200°, as in the case of the red chromoxalate. On ignition in air, it leaves a residue of potassium chromate and chromic oxide.

In the preparation of the red chromomalonate, a second compound crystallising in fine, silky, greenish-blue needles is produced ; the

product is somewhat unstable and has not yet been examined; it is not improbable that this substance is the analogue of the compound forming blue crystals which is produced in the corresponding experiment with the chromoxalic acid mentioned on p. 1444.

I have not deemed it necessary to examine in detail the compounds which chromium forms with the other organic acids, my object being sufficiently secured in establishing their general character and their resemblance to the chromoxalic acid. I shall, therefore, very briefly describe the main facts observed.

#### *Chromic Hydroxide and Tartaric Acid.*

Moist chromic hydroxide is very slowly attacked by a solution of tartaric acid, and after two hours' vigorous boiling only 12·7 per cent. of the theoretical amount of the chromium compound was found to have dissolved. The purplish-red solution was changed to green by caustic alkalis, but chromic hydroxide was not precipitated even by boiling the liquid with an excess of sodium hydroxide for a considerable time.

On evaporation of the original solution, a purplish-red residue is left; when the excess of tartaric acid is removed from this by boiling with alcohol, the product which has now a pale purplish-red colour is found to be quite insoluble in water, even on boiling, but it gradually dissolves again in a solution of tartaric acid.

This compound, dried at 100°, appears to be normal chromium tartrate,  $\text{Cr}_2(\text{C}_4\text{H}_4\text{O}_6)_3$ , the percentage of Cr being 19·22, whereas the formula requires 18·97.

Whereas, judging from the properties of the solution, a chromo-tartaric acid appears to be first formed, this on evaporation decomposes, affording a saline chromium tartrate and free tartaric acid. This behaviour has not been observed with any of the other acids examined.

#### *Chromic Hydroxide and Malic Acid.*

In this case, the proportion of hydroxide dissolved after two hours' boiling amounted to 12·5 per cent. of the theoretical, a greenish-blue dichroic solution being produced, from which the hydroxide is not reprecipitated by boiling with excess of sodium hydroxide.

The solid product, freed from excess of uncombined acid, has a rich green colour and is freely soluble in water affording a strongly acid solution. It is also soluble in alcohol.

The free acid and the ammonium derivative are highly deliquescent; the latter contains the chromium and ammonium in the ratio of four to ten, that is, double that of the corresponding oxalic and malonic compounds.

*Chromic Hydroxide and Glycollic Acid.*

After two hours' boiling, the proportion of hydroxide dissolved amounted to 21.3 per cent. of the theoretical; the purple solution produced is changed to green by alkalis, the hydroxide being re-precipitated on boiling with a slight excess of sodium hydroxide. The dry compound, when purified from excess of acid, is dark green and deliquescent; it yields a strongly acid solution. The ammonium derivative contains its basic radicles in the proportion indicated by  $\text{Cr}_4(\text{NH}_4)_5$ .

*Chromic Hydroxide and Lactic Acid.*

After two hours' boiling, the proportion of hydroxide dissolved amounted to 26.7 per cent. of the theoretical. The solution has a purplish-green colour, with properties similar to the product from glycollic acid.

*Chromic Hydroxide and Citric Acid.*

The proportion of hydroxide dissolved by this acid after two hours' boiling was 25.4 per cent. of the theoretical. The solution has a deep bluish-purple colour, and, as in the case of the tartaric and malic derivatives, the hydroxide is not precipitated by boiling with excess of sodium hydroxide. The dry product freed from excess of acid is dark green, and is freely soluble in water, producing an acid solution with properties similar to those described.

When tricarballic acid was employed instead of citric acid, it was found that, under similar conditions, 15 per cent. of the calculated proportion of chromic hydroxide was dissolved, and a solution was produced with the properties resembling those of the other organic chromic derivatives.

Bearing in mind the main facts which have been recently established in regard to the compounds resulting from the interaction of various metallic hydroxides and the hydroxy-organic acids, I was inclined, when commencing these experiments, to expect some marked difference in the behaviour of chromic hydroxide towards such acids, more particularly in the nature of the products.

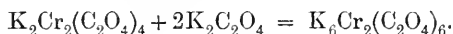
Comparing the action of malic or tartaric acid with that of succinic acid, and the behaviour of citric acid with tricarballic, the hydroxy-acid appears to exert a more powerful solvent action on the chromic hydroxide, but this is by no means general. Acetic\* and propionic acids are well known to dissolve the hydroxide more readily

\* The solution of  $\text{Cr}_2(\text{OH})_6$  in acetic acid has been re-investigated by Recoura (*Compt. rend.*, 1899, 129, 158, 208, 288), who, besides the saline acetate, describes two chromoacetic acids containing the complex  $\text{Cr}(\text{C}_2\text{H}_3\text{O}_2)_2$ .

than I have shown in the case of glycollic and lactic acids. Comparing the behaviour of oxalic, malonic, and succinic acids, the remarkable indifference of chromic hydroxide towards the last-mentioned acid is in striking contrast with the well-marked tendency shown by the hydroxide to react with oxalic acid and the oxalates to form the characteristic stable chromoxalates. Several years ago (*Proc.*, 1887, 3, 142) I pointed out that the oxalic acid group can displace the sulphuric ion in a solution of chromic sulphate with the production of a chromoxalate.

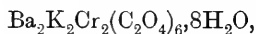
The stability of the chromoxalate is further illustrated in the following unsuccessful attempts to isolate derivatives in which a portion of the oxalic radicle is replaced by some other analogous group.

Crofts showed long ago (*Phil. Mag.*, 1842, 21, 197), that when the red chromoxalate is boiled with a solution of a normal oxalate, a blue chromoxalate is produced, thus :



In my paper (*Trans.*, 1888, 53, 404), I verified this reaction, and mentioned that salts of other organic acids appear to enter into combination with the red chromoxalate.

It would seem not unlikely, for example, that by the interaction of normal potassium succinate and the red chromoxalate a derivative of the composition  $\text{K}_6\text{Cr}_2(\text{C}_2\text{O}_4)_4(\text{C}_4\text{H}_4\text{O}_4)_2$  could be obtained belonging to the blue series, but such, however, is not the case. A peculiar change, proceeding evidently on different lines, occurs, and the blue chromoxalate,  $\text{K}_6\text{Cr}_2(\text{CrO}_4)_6 \cdot 6\text{H}_2\text{O}$ , is the chief product, as shown by the following details. A quantity of the red salt was boiled for half an hour in aqueous solution with two molecular proportions of normal potassium succinate. The red colour of the liquid soon changed to dark bluish-green; the product on concentration continued to yield dark blue crystals of  $\text{K}_6\text{Cr}_2(\text{C}_2\text{O}_4)_6 \cdot 6\text{H}_2\text{O}$  (identified by analyses) until a viscid, syrupy, mother liquor was finally obtained. In the hope of isolating some definite products from this, the diluted mother liquor was treated with an excess of barium chloride, when a small quantity of barium oxalate separated; the filtrate on evaporation furnished a crystalline barium compound having the composition



but beyond this no other definite compound was obtained.

When the red chromoxalate is boiled with potassium acetate or potassium malonate, the blue chromoxalate is likewise the main product.

These salts therefore bring about a peculiar condensation of the red

salt into the blue, with the elimination of some of the chromium-oxalic complex in an uncrystallisable form.

A more complete explanation of this change, together with other points requiring further examination, I shall reserve for a future communication.

#### NOTE ON THE EXISTENCE OF A BORO-OXALATE.

The behaviour of boron hydroxide or boric acid towards the polyhydric alcohols and towards the hydroxy-acids has, from time to time, occupied the attention of several investigators. It now appears to be clearly established that in all these interactions, derivatives are produced by the substitution of hydroxylic hydrogen by the univalent boryl group  $\text{O}\cdot\text{B}\cdot\text{O}$ . The extent of this substitution is conditioned by the number, position, and structural relations of the hydroxyl groups.

The boro-glycerides, boro-tartrates, boro-citrates, and boro-salicylates may be taken as typical examples of this class of compounds, in the solutions of which complex ions containing the boryl group have been recognised.

The extensive investigations of Magnanini (*Gazzetta*, 1891, 21, ii, 215, and 1893, 23, i, 197) on the influence of boric acid on the electrical conductivity of aqueous solutions of organic acids and hydroxyl compounds is particularly interesting. Considering the organic acids only, this chemist, from experiments with a very large number of acids of very varied type, has arrived at the following conclusions :

1. The addition of boric acid to aqueous solutions of hydroxy-acids produces a marked increase in the electrical conductivity, but only when the hydroxyl group is in the  $\alpha$ -position to the carboxyl.

2. The electrical conductivity of acids which do not contain the hydroxyl group in addition to a carboxyl group is never increased by the addition of boric acid to their aqueous solutions.

The behaviour of oxalic acid, for instance, accords with the second conclusion.

Following immediately on Magnanini's work, P. Adam, in a general paper on "The Emetics" (*Compt. rend.*, 1894, 118, 1273), states that oxalic acid and its salts do not combine with boric acid. As far as free oxalic acid and its normal salts are concerned, this statement is quite true, and is in perfect agreement with Magnanini's conclusions. It would thus appear as if a boro-oxalate was not capable of existence, since oxalic acid is not a hydroxy-acid in the accepted meaning of the term.

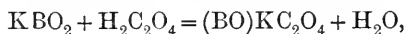
As an outcome of my work on the chromoxalates, I was led, several

years ago, to examine the behaviour of boric acid towards oxalic acid and the oxalates, and also towards malonic and succinic acids, but the results then obtained were not published. I venture, therefore, to record briefly how a well-defined crystalline boro-oxalate may be readily prepared.

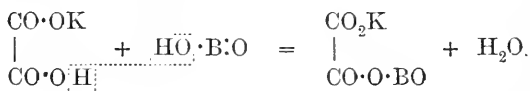
*Preparation of Potassium Boro-oxalate.*

Molecular proportions of potassium metaborate and oxalic acid are boiled together in moderately strong aqueous solution for a short time, 15 to 20 minutes' ebullition sufficing to complete the change when about 50 grams of material are employed. The product separates, on cooling, in rosette-like clusters of minute prisms, and by recrystallisation from a sufficiently dilute solution, brilliant, colourless prisms, 4—5 millimetres in length, may be obtained.

The substance is formed in accordance with the simple equation :



but the crystals thus obtained are more correctly represented by the formula  $\text{K}_2(\text{BO})_2(\text{C}_2\text{O}_4)_2, 3\text{H}_2\text{O}$ . A still more convenient method of preparation consists in boiling a solution of potassium hydrogen oxalate with boric acid, thus :



	Analytical data.		$\text{K}_2(\text{BO})_2(\text{C}_2\text{O}_4)_2, 3\text{H}_2\text{O}$ requires.
	I.	II.	
K .....	21.98	21.51	21.59
Boron.....	6.92 (a)	6.33 (b)	6.07
$\text{C}_2\text{O}_4$ .....	48.92	48.79	48.59
$\text{H}_2\text{O}$ .....	14.99	—	14.90

The water of crystallisation is all expelled at 110—120°. The boron was estimated (a) as  $\text{KBF}_4$  (b) by Gooch's method.

Potassium boro-oxalate is freely soluble in water and almost insoluble in strong alcohol; the aqueous solution has a decided acid reaction.

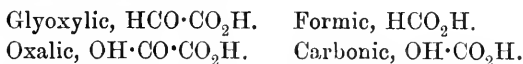
Corresponding salts of sodium and ammonium may be obtained, but they are less stable in solution. I have not been able to obtain definite compounds containing either barium or calcium.

When barium chloride is added to a cold strong solution of the potassium salt, the liquid remains quite clear; on gentle warming, a crystalline precipitate rapidly forms, but although this contains some boron, the oxalic radicle is in large excess, indicating that the sub-

stance is a mixture of barium oxalate with probably some boroxalate.

The next point of interest lies in the fact that similar experiments with malonic and succinic acids fail entirely to give corresponding boron derivatives. When succinic acid is boiled with a solution of a metaborate, or when boric acid is boiled with a solution of potassium hydrogen succinate, unchanged boric acid separates from the solution on cooling, and the same occurs with malonic acid.

The existence of a well-defined boro-oxalate and its method of preparation indicate that in their behaviour towards boric acid the acid oxalates resemble the salts of the hydroxy-acids. This fact is quite in keeping with a view which may be here suggested, that oxalic acid, although itself a dicarboxylic acid, may also be regarded as the first member of a series of hydroxy-acids having the general formula  $R''(\text{OH})\cdot\text{CO}\cdot\text{CO}_2\text{H}$ . Thus oxalic acid bears the same relation to glyoxylic acid as carbonic bears to formic acid:



The second member of the series would be  $\text{CH}_2(\text{OH})\cdot\text{CO}\cdot\text{CO}_2\text{H}$ ; the acids would all contain, like oxalic acid itself, the nucleus  $-\text{CO}\cdot\text{CO}-$ . In the case of oxalic acid, its hydroxylic character only comes into evidence when one of the carboxyl groups has been neutralised.

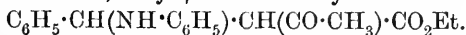
Disregarding the experimental facts which lead to this suggestion, the same view might obviously be extended to malonic acid; in this case, the residual hydroxyl group, after partial neutralisation, would not be in the  $\alpha$ -position, which, as Magnanini (*loc. cit.*) has shown, is necessary for the formation of boron derivatives from acid substances.

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## CXLVI.—*Olefinic Ketonic Compounds.*

By SIEGFRIED RUHEMANN.

RUHEMANN and WATSON (Trans., 1904, 85, 1170), in the course of their research on the formation of additive products of olefinic ketonic compounds with organic bases, have obtained from aniline and ethyl benzylideneacetoacetate, ethyl  $\beta$ -anilinobenzylacetoacetate,



Owing to a printer's error, the melting point was given in this paper

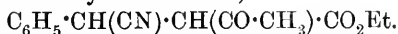
as  $103^{\circ}$  instead of  $105^{\circ}$ . The compound ought to be identical with one of the isomerides which, according to Schiff (*Ber.*, 1898, 31, 215, 601), resulted from the combination of benzylideneaniline with ethyl acetoacetate. Schiff's results were disputed by Rabe (*Ber.*, 1902, 35, 3947), whose investigation induced him to deny the existence of desmotropic modifications of the additive compound. Francis (*Ber.*, 1903, 36, 937), also, repeated Schiff's experiments, and was able to isolate a compound melting at  $107-108^{\circ}$  which corresponded with one of Schiff's isomerides (m. p.  $103-104^{\circ}$ ); moreover, he found that, if the union of benzylideneaniline with ethyl acetoacetate was effected in the presence of piperidine, a substance was produced which melted at a lower temperature. He was, however, unable to isolate it in a pure state, his preparations melting indefinitely at about  $80^{\circ}$ . Morrell and Bellars (*Trans.*, 1903, 83, 1292) likewise investigated this reaction, and their experiments pointed to the existence of one additive product only which melted at  $78^{\circ}$  (compare Francis and Taylor, *Trans.*, 1904, 85, 998).

I did not intend to take part in this discussion, since the melting point of  $105^{\circ}$  (Ruhemann and Watson, *loc. cit.*) found for the additive product of aniline with ethyl benzylideneacetoacetate agreed fairly well with the one given by Francis for ethyl benzylideneanilineacetoacetate. But my attention was drawn to a fact which I had overlooked, namely, that Rabe (*loc. cit.*) had previously effected the combination of aniline with ethyl benzylideneacetoacetate and had thus obtained a compound which melted at  $78^{\circ}$ , instead of  $105^{\circ}$  which we observed. This circumstance induced me to re-examine the reaction, but I obtained the same result as before, the only difference being that it was found possible to raise the melting point of the compound to  $106-107^{\circ}$  after two crystallisations from a mixture of benzene and light petroleum (b. p.  $50-60^{\circ}$ ). I tried in vain to isolate a substance melting at  $78^{\circ}$ . The reason of the failure might probably be found in the fact, observed by Francis (*loc. cit.*), that the more fusible modification readily underwent decomposition when in solution.

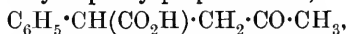
After having studied the behaviour of organic bases towards olefinic ketonic compounds, I have subjected the latter substances to the action of potassium cyanide. Bredt and Kallers (*Annalen*, 1896, 293, 338) had already found that potassium cyanide yielded additive compounds with the ethyl esters of alkylidenemalonic acids, but they were unable to effect a union of hydrogen cyanide with the esters of  $\alpha\beta$ -unsaturated acids. This reaction has since been carefully studied by Lapworth (*Trans.*, 1903, 83, 995; 1904, 85, 1214), who combined hydrogen cyanide with phorone, benzylidenebenzyl cyanide, and mesityl-oxide.

In examining the action of potassium cyanide with olefinic ketonic

compounds, I have found that on using benzylideneacetylacetone the union with the cyanide takes place with the greatest ease and furnishes cyanobenzylacetylacetone,  $C_6H_5 \cdot CH(CN) \cdot CH(CO \cdot CH_3)_2$ . Potassium cyanide combines less readily with ethyl benzylideneacetoacetate, forming ethyl cyanobenzylacetoacetate,

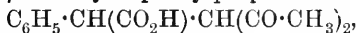


On hydrolysis by alcoholic potash, the former nitrile loses one acetyl group and yields  $\beta$ -acetyl- $\alpha$ -phenylpropionic acid,

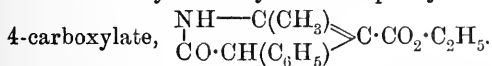


whilst ethyl cyanobenzylacetoacetate is thus transformed into a mixture of  $\beta$ -acetyl- $\alpha$ -phenylpropionic acid and phenylsuccinic acid.

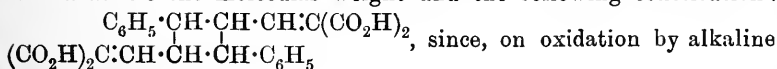
Of special interest is the action of concentrated sulphuric acid on those additive products. Hydrolysis takes place without the loss of the acetyl group from cyanobenzylacetylacetone, or the loss of acetyl or carboxyl from ethyl cyanobenzylacetoacetate. The first nitrile is transformed into  $\beta\beta$ -diacetyl- $\alpha$ -phenylpropionic acid,



and the other yields ethyl 2-keto-3-phenyl-5-methyl-2 : 3-dihydropyrrole-



Besides the record of the research which I have just indicated, this paper contains the result of some experiments which I have undertaken with the view of studying the diolefinic ketonic compounds on similar lines to the corresponding derivatives of the mono-olefines. Since it has been found that benzylideneacetylacetone forms additive compounds with great ease, I have begun the study of cinnamylideneacetylacetone,  $C_6H_5 \cdot CH : CH \cdot CH : C(CO \cdot CH_3)_2$ . This substance may be obtained by the action of piperidine on a mixture of cinnamaldehyde and acetylacetone. On treatment of the diolefinic ketone with phenylhydrazine, a decomposition takes place similar to the one which the mono-olefinic ketones undergo, and yields phenylcinnamylidenehydrazine. I have not yet fully investigated the behaviour of organic bases and potassium cyanide towards cinnamylideneacetylacetone, as the change the substance undergoes on exposure to light has specially occupied my attention. The yellow ketone rapidly becomes converted into a colourless substance which has the same percentage composition, but double the molecular weight. This change is similar to the transformation which Liebermann (*Ber.*, 1895, 28, 1440) observed with cinnamylidenemalonic acid. Riiber (*Ber.*, 1902, 35, 2411), who carefully studied the compound which is formed from cinnamylidenemalonic acid under the influence of light, showed that it had double the molecular weight and the following constitution :



potassium permanganate, it yields oxalic and truxilic acids. It is possible that the substance which I have obtained from cinnamylideneacetylacetone is also a derivative of tetramethylene having the follow-

ing formula : 
$$\text{C}_6\text{H}_5 \cdot \underset{\text{CO} \cdot \text{CH}_3}{\underset{|}{\text{CH}}} \cdot \underset{\text{CO} \cdot \text{CH}_3}{\underset{|}{\text{CH}}} \cdot \text{CH} \cdot \text{C}(\text{CO} \cdot \text{CH}_3)_2$$
, but the fact

that the substance gives a purple coloration with ferric chloride is not in harmony with this constitution. A closer study of this compound is in progress.

#### EXPERIMENTAL.

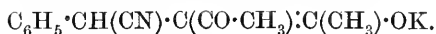
##### *The Union of Aniline with Ethyl Benzylideneacetoacetate.*

In re-examining this reaction, I have mixed 6 grams of the freshly distilled ester with 2.6 grams of aniline ; the mixture becomes warm and in the course of a few hours sets to a hard solid which melts at 81—82°. As this is only sparingly soluble in light petroleum (b. p. 50—60°), it is dissolved in a boiling mixture of this solvent and benzene ; the yellow solution, on cooling, gradually yields colourless needles which melt at 101—102°, and after a second crystallisation from the same mixture at 106—107°. The melting point does not change on repeating the process of crystallisation. Another experiment, performed in a similar manner, has furnished the same result. With the view of ascertaining whether a more fusible substance is produced in the reaction, I have repeatedly washed the crude product with cold benzene. The dry residue melts at 101—102°, and so does the precipitate which is gradually formed on adding light petroleum to the benzene washings. Both specimens, on crystallisation from a mixture of benzene and light petroleum, yield silky needles melting at 106—107°. It may be mentioned that the yield diminishes considerably in the process of crystallisation ; this, most probably, is due to a decomposition of the additive compound, which also takes place when the crystals remain in their mother liquor, because after some days they disappear completely. Similar observations have been made by Francis (*loc. cit.*).

##### *Action of Potassium Cyanide on Olefinic Ketonic Compounds.*

*Cyanobenzylacetylacetone*,  $\text{C}_6\text{H}_5 \cdot \text{CH}(\text{CN}) \cdot \text{CH}(\text{CO} \cdot \text{CH}_3)_2$ .—Hydrogen cyanide or its aqueous solution does not unite with benzylideneacetylacetone ; but a reaction takes place with the greatest ease, accompanied by development of heat, on mixing the ketone (4 grams) dissolved in alcohol with a concentrated aqueous solution of potassium cyanide (4 grams). On adding water, a yellow solution is formed which

contains cyanobenzylacetylacetone in the form of its potassium compound. This substance should no doubt be formulated thus:



Acetic acid or dilute hydrochloric acid precipitates almost the theoretical quantity of the nitrile in colourless needles which, after being well washed and dried in a vacuum over sulphuric acid, melt indefinitely at 120—121°. The substance readily dissolves in hot alcohol, but prolonged boiling is to be avoided, because decomposition takes place, the solution turns red and, on cooling, deposits red plates. In order to crystallise the nitrile, it is gradually added to hot alcohol, and water is then mixed with the filtered solution until crystals begin to separate; after a short time, the whole sets to a semi-solid mass of colourless needles, which then melt at 127—128°.

0.1998 gave 0.5310  $\text{CO}_2$  and 0.1103  $\text{H}_2\text{O}$ .  $\text{C} = 72.48$ ;  $\text{H} = 6.13$ .

0.2078 „ 12.2 c.c. moist nitrogen at 22° and 761 mm.  $\text{N} = 6.65$ .

$\text{C}_{13}\text{H}_{13}\text{O}_2\text{N}$  requires  $\text{C} = 72.56$ ;  $\text{H} = 6.04$ ;  $\text{N} = 6.51$  per cent.

The substance is sparingly soluble in cold alcohol, but readily dissolves in the hot solvent or in chloroform. Ferric chloride gives a red coloration with an alcoholic solution of the nitrile.

#### *Hydrolysis of Cyanobenzylacetylacetone by Caustic Potash.*

Cyanobenzylacetylacetone is very soluble in aqueous caustic potash; on digesting the alkaline solution on the water-bath, a crystalline product is deposited, and ammonia is simultaneously evolved. The solid is insoluble in water, dissolves only sparingly in alcohol, but readily in boiling glacial acetic acid; on adding water to the hot solution until it becomes turbid, yellow prisms separate which melt and decompose at 236°. This substance is *acetylphenylpropionamide*,  $\text{C}_6\text{H}_5\cdot\text{CH}(\text{CO}\cdot\text{NH}_2)\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_3$ .

0.1595 gave 10.6 c.c. moist nitrogen at 20° and 754 mm.  $\text{N} = 7.53$ .

$\text{C}_{11}\text{H}_{13}\text{O}_2\text{N}$  requires  $\text{N} = 7.33$  per cent.

The amide, which is first formed from the nitrile by the action of potash, on boiling with the alkali for 4—5 hours, yields *acetylphenylpropionic acid*,  $\text{C}_6\text{H}_5\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_3$ . This is isolated from the alkaline liquor by adding an excess of dilute hydrochloric acid and extracting with ether. On evaporating off the solvent, the acid remains as a red oil which solidifies when cold. The acid is purified by dissolving the solid in boiling water and decolorising the solution with animal charcoal. From the concentrated filtrate, groups of plates separate which melt at 126°.

0.1998 gave 0.5028  $\text{CO}_2$  and 0.1130  $\text{H}_2\text{O}$ .  $\text{C} = 68.63$ ;  $\text{H} = 6.28$ .

$\text{C}_{11}\text{H}_{12}\text{O}_3$  requires  $\text{C} = 68.75$ ;  $\text{H} = 6.25$  per cent.

This compound is identical with the acid which von Baeyer and Perkin (*Ber.*, 1884, 17, 72) obtained by the action of hydrochloric acid or baryta water on ethyl phenylacetosuccinate.

*Hydrolysis of Cyanobenzylacetylacetone by Sulphuric Acid.*

As already stated in the introduction, diacetylphenylpropionic acid,  $\text{C}_6\text{H}_5 \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{CH}(\text{CO} \cdot \text{CH}_3)_2$ , is produced by dissolving the nitrile in cold concentrated sulphuric acid, leaving the solution overnight, and then adding it gradually to the water. On repeated extraction with ether and subsequent evaporation of the solvent, an oil is left which soon solidifies. This solid dissolves in boiling water, with the exception of a small quantity of a red resin which is removed by filtration. The solution, after being decolorised by animal charcoal and concentrated, deposits bunches of colourless needles which melt to a yellow liquid at  $149\text{--}150^\circ$ .

0.2002 gave 0.4886  $\text{CO}_2$  and 0.1099  $\text{H}_2\text{O}$ .  $\text{C} = 66.56$ ;  $\text{H} = 6.09$ .

$\text{C}_{13}\text{H}_{14}\text{O}_4$  requires  $\text{C} = 66.66$ ;  $\text{H} = 5.98$  per cent.

Diacetylphenylpropionic acid is sparingly soluble in water, ether, or benzene, but readily dissolves in alcohol; it is extremely soluble in ammonia. The neutral solution yields with silver nitrate a gelatinous silver salt, and with copper sulphate a green precipitate. Ferric chloride does not give a coloration with either aqueous or alcoholic solutions of the acid.

*Ethyl Cyanobenzylacetoacetate,  $\text{C}_6\text{H}_5 \cdot \text{CH}(\text{CN}) \cdot \text{CH}(\text{CO}_2 \cdot \text{C}_2\text{H}_5) \cdot \text{CO} \cdot \text{CH}_3$ .*

The union of potassium cyanide with ethyl benzylideneacetoacetate is brought about in the same manner as with the former ketonic compound, by gradually mixing a concentrated aqueous solution of potassium cyanide (10 grams) with the ketonic ester (10 grams) dissolved in alcohol. A development of heat takes place which, however, is not so intense as in the former case. After half an hour, the product is treated with water, when a slight turbidity is produced which may be removed by ether. On adding dilute hydrochloric acid to the aqueous solution, an oil is precipitated which is extracted with ether. Ethyl cyanobenzylacetoacetate, which is left on evaporation of the solvent, is a yellow, viscid oil; its alcoholic solution gives with ferric chloride a purple coloration. The ester cannot be distilled even under diminished pressure. For analysis, it has been dried first in a vacuum over sulphuric acid and soda lime, and finally at  $100^\circ$ .

0.2686 gave 13.8 c.c. moist nitrogen at 22° and 757 mm.  $N = 5.79$ .  
 $C_{14}H_{15}O_3N$  requires  $N = 5.71$  per cent.

*Action of Caustic Potash on Ethyl Cyanobenzylacetoacetate.*

On boiling the oil with aqueous caustic potash until ammonia ceases to be evolved, a red solution is obtained. This is treated with an excess of dilute sulphuric acid and extracted with ether. The solid which is left on evaporation of the solvent is a mixture of acetylphenylpropionic acid and phenylsuccinic acid. These substances may be separated by boiling the product with benzene, which readily dissolves the ketonic acid, leaving almost the whole of the phenylsuccinic acid. The latter crystallises from water in stout needles which melt at 167° and have all the properties characteristic of this acid (see Spiegel, *Annalen*, 1883, 219, 30; Bredt and Kallen, *Annalen*, 1896, 293, 348).

0.2003 gave 0.4535  $CO_2$  and 0.0938  $H_2O$ .  $C = 61.74$ ;  $H = 5.20$ .  
 $C_{10}H_{10}O_4$  requires  $C = 61.85$ ;  $H = 5.15$  per cent.

Acetylphenylpropionic acid has been isolated from the above-mentioned benzene extract by evaporating off the solvent and crystallising the residue from boiling water.

*Action of Sulphuric Acid on Ethyl Cyanobenzylacetoacetate.*

The dihydropyrrole derivative which is formed in this reaction is identical with the lactone of ethyl  $\alpha$ -aminophenylethylidenesuccinate which Emery (*Annalen*, 1890, 260, 154; see also Weltner, *Ber.*, 1885, 18, 795) obtained from ethyl acetylphenylsuccinate. It is prepared from ethyl cyanobenzylacetoacetate by gradually adding the ester to concentrated sulphuric acid, cooled down by cold water. The red solution thus produced is left overnight and then carefully introduced into water, when a yellow solid separates which readily dissolves in alcohol. The alcoholic solution is boiled with animal charcoal, and water added to the hot filtrate until it becomes turbid; on cooling, colourless needles separate which melt at 128—129°, the melting point observed by Emery being 127—128°.

0.2015 gave 0.5066  $CO_2$  and 0.1118  $H_2O$ .  $C = 68.56$ ;  $H = 6.16$ .  
 0.2005 „ 9.6 c.c. moist nitrogen at 16° and 769 mm.  $N = 5.65$ .  
 $C_{14}H_{15}O_3N$  requires  $C = 68.57$ ;  $H = 6.12$ ;  $N = 5.71$  per cent.

To Emery's description of the properties of the compound, I have to add that it dissolves in cold dilute caustic potash and is precipitated unchanged by mineral acids; but ammonia is evolved if the alkaline

solution is boiled. Ferric chloride gives, with an alcoholic solution of the substance, a yellowish-red coloration which first deepens on warming and then changes to light yellow.

*Cinnamylideneacetylacetone*,  $C_6H_5 \cdot CH:CH \cdot CH:C(CO \cdot CH_3)_2$ .

The condensation of cinnamaldehyde with acetylacetone cannot be brought about by means of hydrogen chloride, because, on passing the dry gas into the mixture, cooled down by ice, it darkens and is finally transformed into a tarry product. Cinnamylideneacetylacetone can, however, be obtained on using piperidine instead of hydrogen chloride. If piperidine (5 drops) is added to the mixture of cinnamaldehyde (13.2 grams) and acetylacetone (10 grams), heat is developed and the liquid becomes turbid. After 2—3 days, the whole is transformed into a semi-solid mass, which is washed with cold alcohol and dissolved in the boiling solvent, from which, on cooling, it crystallises in yellow plates melting at 103—104°.

0.2023 gave 0.5818  $CO_2$  and 0.1205  $H_2O$ .  $C = 78.43$ ;  $H = 6.61$ .

$C_{14}H_{14}O_2$  requires  $C = 78.50$ ;  $H = 6.54$  per cent.

The alcoholic washings of the product, when mixed with a few drops of piperidine, furnish a further crop of the same substance. The yield, however, is not satisfactory, because a considerable quantity of an oil remains dissolved in the alcohol. Cinnamylideneacetylacetone dissolves in concentrated sulphuric acid yielding a deep red solution; no coloration is developed on adding ferric chloride to an alcoholic solution of the substance.

It reacts with phenylhydrazine to form phenylcinnamylidenehydrazine, this product separating when the alcoholic solution of the mixture of the ketone and phenylhydrazine is left for a day; it has been identified by the melting point (168°) and by a nitrogen determination:  $N = 12.66$ , whereas  $C_{15}H_{14}N_2$  requires  $N = 12.61$  per cent.

This reaction, therefore, is analogous to the transformation which benzylideneacetylacetone undergoes under the influence of phenylhydrazine (Ruhemann and Watson, *Trans.*, 1904, 85, 466).

#### *Action of Light on Cinnamylideneacetylacetone.*

If finely-powdered cinnamylideneacetylacetone is placed in a thin layer between two glass plates and exposed to direct sunlight, it turns white in the course of a few hours. The white powder, when washed with dilute alcohol and frequently crystallised from methyl or ethyl alcohol, yields colourless needles melting at 158—159°. Analysis

shows that this substance has the same percentage composition as the original yellow compound.

0.2007 gave 0.5778  $\text{CO}_2$  and 0.1185  $\text{H}_2\text{O}$ .  $\text{C} = 78.52$ ;  $\text{H} = 6.56$ .

$\text{C}_{14}\text{H}_{14}\text{O}_2$  requires  $\text{C} = 78.50$ ;  $\text{H} = 6.54$  per cent.

The comparison of the results of the molecular weight determinations proves, however, that the colourless substance has double the molecular weight of the yellow one:

0.3775 cinnamylideneacetylacetone in 20.58 glacial acetic acid gave  $\Delta t = 0.324^\circ$ ; M. W. = 219.7.  $\text{C}_{14}\text{H}_{14}\text{O}_2$  requires M. W. = 214.

The molecular weight of the colourless substance (m. p.  $158-159^\circ$ ) has been determined by Landsberger's method with the following result:

0.2667 in 9.28 ethyl alcohol gave  $\Delta t + 0.08^\circ$ . M. W. = 413.

$(\text{C}_{14}\text{H}_{14}\text{O}_2)_2$  requires M. W. = 428.

The colourless compound is insoluble in water; it dissolves with difficulty in the ordinary organic solvents in the cold, but readily on heating. It is soluble in cold concentrated sulphuric acid yielding an almost colourless solution; this, however, gradually becomes red, but does not assume the deep colour which is formed at once on adding the acid to cinnamylideneacetylacetone. The colourless substance differs, also, from the yellow compound inasmuch as its alcoholic solution gives with ferric chloride a purple coloration, whilst, as stated before, cinnamylideneacetylacetone does not yield a coloration with the chloride.

GONVILLE AND CAIUS COLLEGE,  
CAMBRIDGE.

## CXLVII.—*The Colouring Principle of the Flowers of the Butea Frondosa.*

By ARTHUR GEORGE PERKIN, F.R.S., and, in part, the late JOHN JAMES HUMMEL.

THE *Butea frondosa*, also called *Dhak* or *Pulas*, is a fine tree, thirty to forty feet high, belonging to the order *Leguminosæ*; it is common throughout India and Burma, and is found in the North-West Himalaya as far as the Jhelum River. The flowers, which, in the

dried condition, are known as *tísú*, *késú*, *kesuda*, or *palás-képpál*, have a bright orange colour, and, although they are much larger, closely resemble in appearance the common gorse flower (*Ulex europæus*), with which, indeed, they are botanically allied. An almost unlimited supply of these flowers can be obtained, and large quantities are collected in March and April, dried in the sun, and employed by the natives to produce a yellow dye, much used during the Holi festival. The dyeing operation, which consists of steeping the material in a hot or cold decoction of the flowers, is virtually a process of staining, because the colour can be readily washed out, and this is, indeed, considered an advantage and is frequently effected at the end of the festival. On the other hand, a more permanent result is sometimes produced either by first preparing the cloth with alum and wood-ash or by adding these substances to the dye-bath. Occasionally other dyes are employed along with the flowers, such as annatto, turmeric, or myrabolans, either with the object of modifying the colour obtained or to render it less fleeting. From the *Butea frondosa* is also obtained the so-called "Butea gum" or "Bengal kino" employed by the natives for tanning leather, and the tree is of additional interest because in many parts of India the lac insect (*Coccus lacca*) is reared on it. This, as is well known, causes the formation of stick lac, from which shellac and lac dye are prepared.

A preliminary examination of these flowers was made some years ago by Hummel and Cavallo (Proc., 1894, 10, 11), who isolated a substance which they termed butein, to which they assigned the formula  $C_{15}H_{14}O_5$ , supposing this substance to be the true colouring matter. This product, which was present in the plant in the form of glucoside, in some respects yielded shades which were not unlike those of the fisetin obtained from young fustic. More recently, Hill (Proc., 1903, 19, 133), who, although aware that the subject had been previously studied, had not access to the original papers, extracted from these flowers a colouring matter in the form of small, lemon-yellow crystals which gave the reactions of fisetin. He noted further the presence of a tannin matter which readily yields a phlobophane, and found that the latter, on fusion with potassium hydroxide, gave phloroglucinol and protocatechuic acid.

For a liberal supply of the raw material, we are indebted to the authorities of the Imperial Institute.

#### EXPERIMENTAL.

The most rapid method for the isolation of the colouring principle is that originally employed by Hummel and Cavallo (*loc. cit.*), and consists in digesting an aqueous decoction of the flowers at the boiling

point with a little sulphuric acid to hydrolyse the glucoside, and extracting the product with ether. For this process, very large quantities of ether were necessary, and the following more economical method was therefore devised.

One thousand grams of the flowers were digested for six hours with boiling water, and the extract treated with 50 c.c. of sulphuric acid and again heated for one hour. A light, viscous precipitate, devoid of dyeing property, had then separated, and this was removed while hot, and the filtrate left overnight. The clear liquid was now decanted from a small quantity of tarry substance (A), which was reserved for further examination, and gently evaporated for three hours on the water-bath. A further quantity of a black, viscous product was thus deposited, and when this had been removed the filtrate, after some days, deposited crystals, the yield of which was usually from 18 to 20 grams or approximately 2 per cent., but varying according to the prevailing temperature. Again, if the evaporation was carried too far, a destruction of the colouring principle appeared to ensue and the quantity isolated was small. For purification, the product was dissolved in a little alcohol, the mixture poured into ether, and the solution repeatedly agitated with water until the washings were no longer of a dark colour. The ethereal liquid was evaporated, the residue dissolved in hot alcohol, the solution treated with a very little boiling water, and the substance which separated on cooling recrystallised in a similar manner until pure. After drying at  $160^{\circ}$ , an analysis gave the following result:

Found, C = 66.00; H = 4.56.

$C_{15}H_{12}O_5$  requires C = 66.17; H = 4.41 per cent.

For this substance, the name *butin* is now proposed in preference to the term *butein* originally assigned to it, because, as will be seen later on, it is not the true colouring matter, but rather the colouring principle from which the dye is derived.

When thus obtained, butin crystallises in small, colourless needles melting at  $224-226^{\circ}$ , but if much water be employed for its separation the crystals then have a pale yellow tint. The air-dried product usually contains  $\frac{1}{2}H_2O$ , which is evolved at  $160^{\circ}$ .

Found,  $H_2O = 3.23$ .  $C_{15}H_{12}O_5, \frac{1}{2}H_2O$  requires 3.20 per cent.

But, on the other hand, if butin is crystallised from boiling water, in which it is sparingly soluble, it is deposited in pale yellow leaflets having the formula  $C_{15}H_{12}O_5, 2H_2O$ .

Found,  $H_2O = 11.33$ ; 11.79.  $C_{15}H_{12}O_5, 2H_2O$  requires 11.68 per cent.

It sometimes happens, however, that both these forms are produced

from the same solution, in which case the compound  $C_{30}H_{24}O_{10} \cdot H_2O$  is first deposited.

Butin is readily soluble in alcohol, somewhat more sparingly so in acetic acid or ether, and almost insoluble in benzene. With alcoholic lead acetate it gives a pale yellow, almost colourless precipitate, and with alcoholic ferric chloride a deep green liquid is produced. When treated with cold sulphuric acid, it does not at first dissolve, but assumes a deep red colour as if an acid compound was produced; this subsequently passes into solution with the formation of a pale yellow liquid. With acetic and sulphuric acids, however, no crystalline acid compound separates, and alcoholic potassium acetate does not cause the deposition of a mono-potassium salt. Butin does not contain methoxy-groups.

*Acetylbutin* may be prepared in the usual manner by means of acetic anhydride and sodium acetate, but as viscous by-products are simultaneously produced, a modification of Deninger's benzoylation process was chiefly employed. Two grams of butin dissolved in 30 grams of pyridine were mixed with 10 grams of acetyl chloride, and after one hour the mixture was poured into water, the insoluble residue washed several times by decantation, and dissolved in a mixture of acetone and alcohol. Crystals gradually separated which were purified by recrystallisation from the same solvents.

Found, C = 63.35; H = 4.87.

$C_{15}H_9O_5(C_2H_3O)_3$  requires C = 63.32; H = 4.52 per cent.

A molecular weight determination by the cryoscopic method gave the following result:

0.2390 in 13.15 naphthalene gave  $\Delta t = 0.31^\circ$ ; M. W. = 410.

$C_{21}H_{15}O_8$  requires M. W. = 398.

The acetyl determination was carried out by the method previously described (Proc., 1904, 37, 171), employing (a) alcoholic sulphuric acid, and (b) alcoholic potassium acetate.

Found, acetic acid (a) = 45.34, 45.60, and (b) = 45.60.

$C_{15}H_9O_5(C_2H_3O)_3$  requires  $C_2H_4O_2$  = 45.22 per cent.

Acetylbutin crystallises in colourless leaflets melting at  $123-125^\circ$ , readily soluble in hot alcohol.

*Benzoylbutin*, which is readily prepared by Deninger's method, employing 2 grams of butin, 30 grams of pyridine, and 23 grams of benzoyl chloride, was isolated in the usual manner and crystallised from a mixture of benzene and alcohol.

Found, C = 74.02 ; H = 4.05.

$C_{15}H_9O_5(C_7H_5O)_3$  requires C = 73.97 ; H = 4.10 per cent.  
0.3615 in 13.99 naphthalene gave  $\Delta t = 0.31^\circ$  ; M. W. = 583.

$C_{36}H_{24}O_8$  requires M. W. = 584.

Tribenzoylbutin forms colourless needles melting at  $155-157^\circ$ , sparingly soluble in alcohol. These results therefore indicate that butin has the formula  $C_{15}H_{12}O_5$  and contains three hydroxyl groups.

On fusion with caustic potash and a little water at  $200-220^\circ$  butin gives protocatechuic acid (m. p.  $194-196^\circ$ ) and resorcinol (m. p.  $107-109^\circ$ ).

*The Conversion of Butin into the Colouring Matter Butein.*

Butin dissolves readily in cold alkaline solutions, forming a pale, orange-red liquid, which, when at once acidified, deposits the unchanged substance. On boiling the solution in potassium hydroxide, however, the colour rapidly darkens, and if acid is now added a bright orange, crystalline precipitate almost immediately separates, which is rapidly collected and washed with boiling water. The filtrate, on cooling, deposits unattacked butin, but if this is again made alkaline and heated to boiling a further quantity of the new substance may be thus obtained. The product was further purified by crystallisation from dilute alcohol and dried at  $160^\circ$ .

Found, C = 66.26 ; H = 4.66.

$C_{15}H_{12}O_5$  requires C = 66.17 ; H = 4.41 per cent.

This substance, to which the name *butein* is assigned, forms glistening, reddish-orange needles melting at  $213-215^\circ$  ; when deposited from dilute alcohol, it contains water of crystallisation which can be removed at  $100^\circ$ .

Found,  $H_2O = 6.26$ .  $C_{15}H_{12}O_5 \cdot H_2O$  requires  $H_2O = 6.21$  per cent.

If butin is digested with boiling alcoholic potassium acetate for some time, butein is produced in small quantity, and this change appears also to occur slowly when a boiling alcoholic solution of butin is treated with a little dilute sulphuric acid. Boiling alcoholic potash also behaves in a similar manner, but somewhat less energetically than the aqueous alkali.

Butein is readily soluble in alcohol and to some extent in ether, but is much more sparingly soluble than butin in hot water, a fact which is of assistance in separating these two substances ; it dissolves in alkaline solutions to a deep orange-red solution, and with a similar tint in boiling alcoholic potassium acetate, but no insoluble monopotassium salt is thus formed. Alcoholic lead acetate gives a deep red precipitate, and alcoholic ferric chloride an olive-brown coloration. In

cold sulphuric acid it is sparingly soluble forming an orange solution, and the suspended substance assumes the same colour; this indicates the formation of an acid compound, for on dilution with water the colour is discharged and the butein reprecipitated in an unchanged condition. It is energetically attacked by nitric acid (sp. gr. 1.42), a deep brown liquid being thus produced.

*Acetylbutein* is best prepared by the pyridine method, employing the same proportions as were serviceable in the case of acetylbutin. The product crystallised from alcohol in extremely pale yellow or almost colourless needles melting at 129—131°.

Found, C = 62.54; H = 4.79.

$C_{15}H_8O_5(C_2H_3O)_4$  requires C = 62.72; H = 4.55 per cent.

0.4287 in 13.64 naphthalene gave  $\Delta t = 0.47^\circ$ . M. W. = 467.

$C_{23}H_{20}O_9$  requires M. W. = 440.

The acetyl groups were determined by Liebermann's method, for this was possible on account of the sparing solubility of butein in water. The acetic acid was also estimated by the method employed with acetylbutin.

Found, butein = 61.61; acetic acid = 54.

$C_{15}H_8O_5(C_2H_3O)_4$  requires  $C_{15}H_{12}O_5 = 61.81$ ;  $4C_2H_4O_2 = 54.54$  per cent.

It is therefore evident that butein has the same formula as butin, but, on the other hand, whereas butin contains three hydroxyls, in butein four such groups are present.

An attempt to prepare a crystalline benzoylbutein was not successful, the product being of a viscous nature.

*The Action of Alkalis on Butein.*—When fused with caustic potash at 200—220°, butein gives the same products as butin, namely, resorcinol and protocatechuic acid. It was of interest to determine whether some more complex product of the hydrolysis could be obtained by a less energetic action of the alkali, as some further insight into the constitution of the substance might be thus obtained.

Two grams of butein dissolved in 50 c.c. of 50 per cent. aqueous caustic potash were boiled until the orange-red colour of the liquid had become brown, and a sample, when neutralised with acid, no longer gave a precipitate of unchanged substance. The solution was now diluted with water, acidified, extracted with ether, and the oily product dissolved in a little dilute caustic potash; this was then saturated with carbon dioxide, again extracted with ether, and the extract evaporated to dryness. The residue was purified by two or three crystallisations from benzene with the aid of animal charcoal.

Found, C = 62.84; H = 5.40.

$C_8H_8O_3$  requires C = 63.15; H = 5.26 per cent.

This substance melted at 140—143° and had all the properties of resacetophenone.

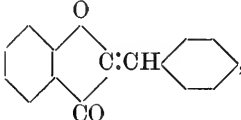
The aqueous liquid from which the resacetophenone had been isolated contained a second substance which was found to consist of protocatechuic acid.

No attempt was made to hydrolyse butin in this manner, for as it was evident that the first action of the alkali would lead to the production of butein, the same final products must result in both cases.

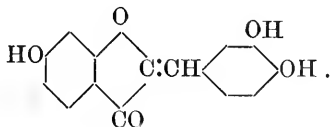
*The Dyeing Properties of Butin and Butein.*—As butin gives with alcoholic lead acetate an almost colourless precipitate, it cannot be regarded as a colouring matter, whereas the behaviour of butein in this respect (*loc. cit.*) is evidence of its intense tinctorial property. In other words, butin is the colouring principle and butein the colouring matter, and their relationship to one another is therefore somewhat analogous to that which exists between hæmatoxylin and hæmatein, and between brazilin and brazilein. It was interesting to find, however, that butin and butein dyed mordanted woollen cloth in identical shades, and this gave rise, in the earlier stages of this work, to the supposition that butein was merely the quinonoid form of butin. That this is hardly the case will be seen later, but it is nevertheless quite certain that by the action of the mordant butin is converted into butein, and is not to be regarded as a colouring matter itself. The following shades were obtained :

Chromium.	Aluminium.	Tin.	Iron.
Reddish-brown.	Brick-red.	Full yellow.	Brownish-black.

These colours differ somewhat in character from those given by any known natural colouring matter, although they bear some resemblance to those furnished by quercetin, myricetin, and fisetin, especially as regards the latter compound. On the other hand, these dyeings are strikingly similar to those yielded by some of the

phenylketocumaran colouring matters, , arti-

ficially prepared by Friedlander and Rudt (*Ber.*, 1896, 29, 879). Although similar in many respects, butein is, however, not identical with the compound :



*Methylation of Butin.*

In the earlier experiments, this operation was carried out in the ordinary way by employing 5 grams of butin, 5 grams of potassium hydroxide in methyl alcohol, and excess of methyl iodide. Subsequently, methyl sulphate was employed, for not only was the action more rapid but a better yield resulted, the products being the same in both cases.

In carrying out the reaction, 10 grams of butin in methyl alcohol were treated with 6.6 grams of potassium hydroxide, and the quantity of methyl sulphate necessary to neutralise the alkali then added. As soon as the reaction had ceased, similar quantities of methyl sulphate and alkali were added for a second and third time. The product was poured into water, the mixture extracted with ether, the ethereal liquid washed with dilute caustic potash solution to remove a trace of partially methylated product, and then evaporated to dryness. A solution of the residue in boiling alcohol slowly deposited crystals, and these, on examination, were found to consist of two substances: (*A*) sparingly soluble in alcohol, and (*B*) which is much more readily so. The yield of the mixture was 5 grams.

The substance (*A*) was purified by frequent crystallisation from alcohol.

Found, C = 68.88 ; H = 6.07.

$C_{15}H_9O_2(O\cdot CH_3)_3$  requires C = 68.79 ; H = 5.73 per cent.

Thus obtained it formed glistening, yellow leaflets melting at 156—158°, sparingly soluble in the usual solvents. If it is dissolved in hot concentrated alcoholic potash, this solution, on cooling, becomes semi-solid owing to the evaporation of a potassium salt which dissolves on treating the mixture with water, and from which the unchanged ether is redeposited on acidification. The addition of one drop of sulphuric acid to a solution of the substance in acetic anhydride causes the formation of a beautiful magenta-coloured liquid.

The second product (*B*) separated in needles, which on close examination appeared to be a mixture, for, whereas some were colourless, others had a yellow tint. By repeated fractional crystallisation and by rejecting the first portions this coloured impurity was gradually removed, but its complete separation was exceedingly troublesome. It was not, however, present in large amount, for the frequent purification did not alter the melting point to any marked extent.

Found, C = 68.54 ; H = 5.95.

$C_{15}H_9O_2(O\cdot CH_3)_3$  requires C = 68.79 ; H = 5.73 per cent.

When thus obtained, it consisted of thin plates melting at  $119-121^{\circ}$ , and gave, with acetic anhydride and sulphuric acid, the same magenta coloration as in the case of substance (A).

The formation of two trimethyl ethers, having the same composition, by the methylation of butin is, at first sight, somewhat remarkable, but this result is more easily understood on considering the behaviour of butin itself with dilute alkaline solutions, whereby it is converted into butein. This reaction would no doubt occur to some extent during the methylation process, and the two products should consist respectively of the trimethyl ethers of butin and butein. For a variety of reasons, it appeared evident that the colourless substance (B) melting at  $119-121^{\circ}$  was the butin derivative, and it was interesting to determine, as a possible confirmation of this point, whether it would be converted by means of alkali into the more sparingly soluble compound (A) melting at  $156-158^{\circ}$ .

Butin trimethyl ether 1.5 grams were dissolved in 15 c.c. of normal alcoholic potash, and the solution was boiled for a few minutes alone, and subsequently with the addition of an equal volume of water. The product was diluted with water, neutralised with acid, and the precipitate which separated was collected and crystallised from alcohol. It formed yellow leaflets melting at  $156-158^{\circ}$ , gave on analysis C=68.96, H=5.96 per cent., and evidently consisted of the butein trimethyl ether (A).

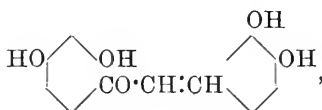
When methylated therefore in the foregoing manner, butin yields both butin and butein trimethyl ethers, and the former can be readily converted into the latter by means of potassium hydroxide solution.

#### *Methylation of Butein.*

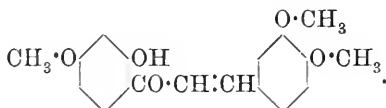
The methylation of butein was now studied by the aid of processes similar to those employed with butin. The results were interesting, for not only was the expected butein trimethyl ether (m. p.  $156-158^{\circ}$ ) obtained, but it was accompanied in all cases by the butin trimethyl ether (m. p.  $119-121^{\circ}$ ). It appeared possible at first that the butein employed was contaminated with butin, but this was evidently not the case, for a sample of the colouring matter specially purified on this account gave an identical result. The yield of butin trimethyl ether was greatest when methyl iodide was employed for the methylation, and but little was obtained if strong aqueous potassium hydroxide was added during methylation with methyl sulphate.

*Synthesis of Butein Trimethyl Ether.*

As butein on hydrolysis gives resacetophenone and protocatechuic acid, it might, if these data alone were considered, be either a flavone or benzylidenecumaran derivative, but its colour reactions, and especially the fact that it contains four hydroxyl groups, render these suppositions untenable. The only constitution for butein in harmony with its properties appeared to be that of a *tetrahydroxybenzylideneacetophenone* having the following formula :



and this has been found correct. Although Kostanecki and his colleagues have employed numerous compounds of this class in the form of their methyl and ethyl ethers during their extremely interesting syntheses of flavanol derivatives (*loc. cit.*), yet a trimethoxyhydroxybenzylideneacetophenone which was suspected to be identical with butein trimethyl ether had not been described :



Molecular proportions of resacetophenone methyl ether and veratraldehyde were condensed in the presence of alcoholic potash, the product dissolved in water, the solution neutralised with acid, and the yellow precipitate collected and purified by crystallisation from alcohol.

Found, C = 68.75 ; H = 6.02.

$\text{C}_{15}\text{H}_9\text{O}_2(\text{O} \cdot \text{CH}_3)_3$  requires C = 68.79 ; H = 5.73 per cent.

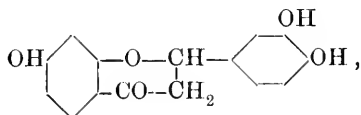
It consisted of orange-yellow leaflets melting at 156—158°, and was identical in all respects with the butein trimethyl ether obtained from natural sources. With acetic anhydride and sulphuric acid, it gave the characteristic magenta coloration.

Butein is accordingly 2 : 4 : 4' : 5'-*tetrahydroxybenzylideneacetophenone* or 2 : 4 : 4' : 5'-*tetrahydroxychalkone*.

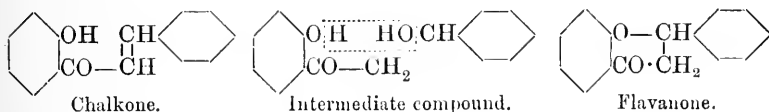
*Synthesis of Butin Trimethyl Ether.*

Butin differs from butein in containing only three hydroxyl groups, a fact which was of extreme importance in elucidating its constitution. That in butin the catechol hydroxyls are both intact appeared likely from the fact that it is precipitated by lead acetate as described above,

and consequently it seemed certain that in this substance a hydroxyl of the resorcinol nucleus was involved in the formation of an anhydride, thus necessitating the production of a ring. Again, the fact that butin was not a colouring matter indicated the absence of the ethylenic linkage which occurs in butein. A consideration of these points and the fact that butin and butein have identical formulæ rendered it necessary to assume that during the reaction by which the latter is converted into the former an intermediate stage must first occur. It therefore seemed probable that butin was a flavanone compound :



a class of substance recently discovered and synthetically prepared by Kostanecki and his colleagues (*Ber.*, 1904, 37, 784, 773, 779), who have shown that chalkone derivatives, on prolonged digestion with dilute sulphuric acid, are partly converted into the corresponding flavanone derivatives, the reaction apparently taking place in the following manner :



The flavanone methyl ethers have been shown by these authors to be colourless, which is also the case with the butin methyl ether under discussion.

In accordance with the method employed by these chemists, artificial butein trimethyl ether was digested for several hours with 10 per cent. sulphuric acid, sufficient alcohol being present to bring the substance into solution. The product, when crystallised from alcohol, deposited first some quantity of the unattached chalkone, but subsequently a more soluble compound separated. After numerous crystallisations, this substance was obtained in an almost colourless condition, and then melted at 118—120°. It was identical with the butin trimethyl ether prepared by methylating butin itself, which must therefore be the 3:4':5'-*flavanone*, the formula of which is given above. On digestion with alcoholic potash and a little water, the artificial butin methyl ether behaved in a similar manner to the natural product, giving butein methyl ether.

*Conversion of Butein into Butin.*—Experiments were now carried out to determine whether butein could be reconverted into butin in a similar manner. Butein (1.5 grams) dissolved in 50 c.c. of 50 per cent. alcohol was treated with 2 c.c. of sulphuric acid and the mixture

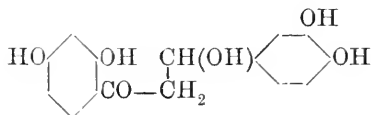
digested on the water-bath for eight hours. The hot liquid, on cautious dilution with boiling water, gave a precipitate of unaltered butein, which was removed, and the filtrate was treated with more water and left overnight. A quantity of pale yellow needles which had then separated was collected and recrystallised from much boiling water in the presence of animal charcoal. The air-dried product had the formula  $C_{15}H_{12}O_5 \cdot 2H_2O$ , melted at  $224-226^\circ$ , and was evidently identical with butin.

Found,  $H_2O = 11.33$ . Found (at  $160^\circ$ ),  $C = 66.17$ ;  $H = 4.41$  per cent.

Aqueous potassium hydroxide reconverted the butin thus prepared into butein. The special behaviour of the flavanone butin with alkaline solutions, by which it is converted into the corresponding chalcone, will probably be found to be characteristic of the whole group; as, however, numerous artificial compounds of this class are under investigation by Kostanecki, the subject has not been further studied in this direction.

The ease with which butin is converted into butein and *vice versa* is very interesting and is worthy of further study from a quantitative standpoint.

This change is readily explained if it is assumed that the intermediate compound (Kostanecki, *loc. cit.*)



is the first product of the reaction in each case, and that this subsequently, by loss of water, passes into either chalcone or flavanone, or both. It is possible that in no case does the reaction become entirely unidirectional, and it is interesting to notice that a trace of butein has always been found among the products of the hydrolysis of acetylbutin with alcoholic sulphuric acid.

Butein and butin are the first members of the chalcone and flavanone groups which have been isolated from natural sources.

Hill's suggestion (*loc. cit.*) that a colouring matter resembling the fisetin of young fustic is contained in the flowers of the *Butea frondosa* made a search for this substance desirable, and its presence was, indeed, possible because, on account of its sparing solubility in water, it would be deposited with the viscous matter so abundantly produced during the isolation of butin. Should fisetin be present, the constituents of this plant would be of special interest, for it would

then be known to contain the chalkone, the flavanone, and the flavone compounds, illustrating the synthesis carried out by Kostanecki (*Ber.*, 1904, 37, 784). An alcoholic solution of the tarry product (4) was poured into ether, the ethereal liquid well washed and evaporated to dryness. The treacly residue was extracted with boiling water, the extract allowed to cool, and the crystals, which slowly separated, were collected, washed with a little ether, and crystallised from dilute alcohol. The substance formed orange-red needles melting at 213—215°, identical in all respects with butein. By this method, the yield of the colouring matter from a kilogram of the flowers was 0.4 gram, and, although some slight loss would occur during its extraction, the quantity actually present in the plant could not far exceed this amount. It is not certain whether butein or its glucoside exists in the fresh flowers; such may be the case, although it is quite possible that this colouring matter has been merely derived from the butin during the operations involved in the extraction of the latter. Fisetin does not therefore appear to exist in the flowers of the *Butea frondosa*.

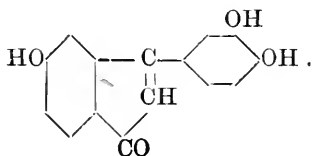
*Action of Sulphuric Acid on Butein.*

If a thin paste of butein with acetic acid is treated in the cold with a few drops of sulphuric acid, the mixture becomes orange-red, and, after a few minutes, minute, dull red needles having a steel-blue iridescence separate out. This substance, which is evidently the sulphuric acid compound of butein, is too unstable for isolation, and on washing with acetic acid is reconverted into butein and sulphuric acid.

When butein (0.25 gram) in 5 c.c. of acetic acid is boiled with four drops of sulphuric acid, the orange-red liquid becomes duller in colour and a new substance gradually separates; this adheres to the sides of the vessel and has a beetle-green iridescence. It is very sparingly soluble in the usual solvents, dissolves in alkaline solutions with a deep blue colour, and under the microscope possesses a distinctly crystalline structure. The acid liquid decanted from this substance on dilution with water deposits a brown precipitate also soluble in alkalis with a bluish-violet coloration, and which dyes mordanted calico with shades of a similar character to those yielded by anthragallol. It appears likely that this more soluble substance represents the first product of the reaction and is subsequently converted into the foregoing dark compound.

A consideration of the formula of butein renders it unlikely that these new substances are anthraquinone derivatives; on the other hand, it is suspected that the formation of a ring takes place with the

abstraction of water, an indone derivative of the following type being the first product :



It is likely that other chalcone derivatives will behave in a similar manner, and the subject is reserved for further examination. Experiments with butin show that in this respect it closely resembles butein, and it is possible that the products thus obtained are identical in both cases.

*The Dyeing Properties of the Flowers.*

Towards mordanted calico, these flowers are almost inert, evidently because the glucoside of butin which they contain is of too stable a character to be hydrolysed by the mordant. In wool dyeing where acid baths are employed, a better result is obtained, although in this case the shades possess but little strength. If the glucoside is first hydrolysed by boiling the flowers with dilute hydrochloric acid and the mixture evaporated to dryness, or if sulphuric acid is employed, and the acid then neutralised with sodium carbonate, a material is obtained which dyes readily by the usual methods. Such products gave the following shades: with chromium, deep terra-cotta; with aluminium, a bright orange; with tin, bright yellow; and with iron, a brownish-olive. The chromium colour is characteristic and is much redder in tint than that yielded in this way by any known natural yellow dye. These colours are somewhat fugitive to light, and the *Butea frondosa* flowers cannot therefore be classed among the more valuable natural yellow colouring matters.

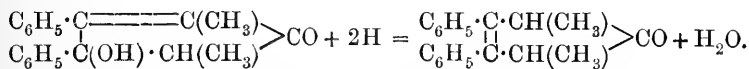
The expenses of this research have been partly defrayed by a grant received from the Research Fund of the Chemical Society.

THE CLOTHWORKERS' RESEARCH LABORATORY,  
DYEING DEPARTMENT,  
THE UNIVERSITY, LEEDS.

CXLVIII.—*Reduction Products of  $\alpha\beta$ -Dimethylanhydracetonebenzil, and Condensation Products of Benzaldehyde with Ketones.*

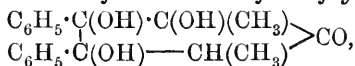
By FRANCIS ROBERT JAPP, F.R.S., and WILLIAM MAITLAND, B.Sc.,  
Carnegie Fellow in the University of Aberdeen.

WE find that when  $\alpha\beta$ -dimethylanhydracetonebenzil (compare Japp and Burton, *Trans.*, 1887, 51, 432; Japp and Meldrum, 1901, 79, 1036) is boiled for five minutes with fuming hydriodic acid, it is reduced to 4:5-diphenyl-1:3-dimethylcyclopenten(4)-one(2), melting at  $122^\circ$ :

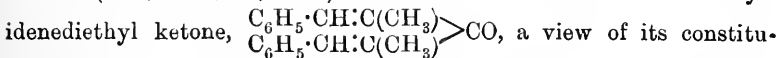


This change in the position of the double bonds is of general occurrence in the reduction of anhydracetonebenzil derivatives to cyclopentenones (compare Japp and Murray, *Trans.*, 1897, 71, 145; Japp and Meldrum, 1901, 79, 1026).

The foregoing product is identical with the substance of the same melting point obtained, along with other compounds, by the reduction of 4:5-diphenyl-1:3-dimethyl-1:4:5-trihydroxycyclopentanone(2),

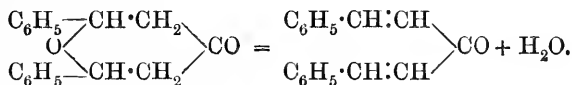


with hydriodic acid (Japp and Michie, *Trans.*, 1903, 83, 303). It is, moreover, identical with the compound to which Vorländer and Wilcke (*Ber.*, 1898, 31, 1887) ascribe the constitution of a dibenzylidenediethyl ketone,



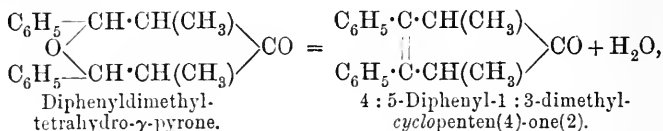
a view of its constitution which, as we shall now show, must be abandoned, as the reactions of the compound prove that it contains the cyclopentenone group.

Petrenko-Kritschenko and Plotnikoff (*Ber.*, 1897, 30, 2801) had obtained dibenzylideneacetone by warming an alcoholic solution of diphenyltetrahydro- $\gamma$ -pyrone to which a few drops of hydrochloric acid had been added:



Vorländer and Wilcke (*loc. cit.*) tried whether the same treatment would convert Vorländer and Hobohm's diphenyldimethyltetrahydro- $\gamma$ -pyrone (*Ber.*, 1896, 29, 1352) into dibenzylidenediethylketone, but found that under these conditions no change occurred. However, by

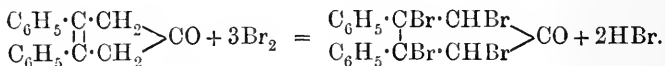
passing gaseous hydrogen chloride for two hours into a boiling solution of diphenyldimethyltetrahydro- $\gamma$ -pyrone in glacial acetic acid and allowing the mixture to remain for some days, they succeeded in transforming this substance into a compound having the expected composition, which they regarded as dibenzylidenediethyl ketone. Under this more drastic treatment, however, the  $\gamma$ -pyrone derivative is dehydrated, not on the lines of Petrenko-Kritschenko and Plotnikoff's reaction, as Vorländer and Wilcke assume, but according to the scheme:



the carbon chain closing in the process.

Vorländer and Wilcke (*loc. cit.*) believed that they had obtained confirmation of their view as to the constitution of the foregoing compound in the fact that it yields with bromine a substance which they regarded as dibenzylidenediethyl ketone tetrabromide. This bromine derivative, however, is only partly additive; it is *diphenyldimethyl-dibromocyclopentenone dibromide*, or better, *diphenyldimethyltetrabromocyclopentanone*,  $\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{CBr} \cdot \text{CBr}(\text{CH}_3) \\ \parallel \\ \text{C}_6\text{H}_5 \cdot \text{CBr} \cdot \text{CBr}(\text{CH}_3) \end{array} \rangle \text{CO}$ . Hydrogen bromide is evolved during its formation, and it contains in its molecule 2 atoms of hydrogen fewer than would be required by the formula ascribed to it by Vorländer and Wilcke.

We have ascertained that diphenylcyclopentenone interacts in a similar manner with bromine, yielding *diphenyltetrabromocyclopentanone*:



Vorländer and Mumme (*Ber.*, 1903, 36, 1477) found that the supposed dibenzylidenediethyl ketone, unlike dibenzylideneacetone and other doubly unsaturated ketones of this type, did not form an additive compound with hydrogen chloride. The explanation lies in the fact that it differs entirely in constitution from these.

Again, Mentzel (*Ber.*, 1903, 36, 1499) draws certain theoretical conclusions from the facts (1) that the supposed dibenzylidenediethyl ketone is "almost colourless" (it is quite colourless when pure) and (2) that it gives hardly any coloration with concentrated sulphuric acid. He seeks to explain its apparently exceptional behaviour in these respects, compared with that of various authentic dibenzylidene derivatives of ketones. No explanation is necessary; its behaviour

is that of the other *cyclopentenones* obtained by the reduction of anhydrazetonebenzil and its derivatives.

Although the description which Petrenko-Kritschenko and Plotnikoff (*loc. cit.*) give of the compound  $C_{17}H_{14}O$ , which they prepared by the action of alcoholic hydrochloric acid on diphenyltetrahydro- $\gamma$ -pyrone, left little doubt that this substance was, as they assert, dibenzylideneacetone, and not the isomeric diphenyl*cyclopentenone*, we nevertheless repeated their experiment, as the nearness of the melting points of the two isomerides—dibenzylideneacetone  $112^\circ$ , diphenyl*cyclopentenone*  $110^\circ$ —rendered just possible a confusion between the two substances. We found, however, that the product was undoubtedly dibenzylideneacetone, a result which we confirmed by the mixture melting-point test.

By boiling diphenyldimethyl*cyclopentenone* (m. p.  $122^\circ$ ), prepared by Vorländer and Wilcke's method, with hydriodic acid and red phosphorus for  $1\frac{1}{2}$  hours, it is reduced to 4:5-diphenyl-1:3-dimethyl*cyclopentanone*(2), 
$$\begin{array}{c} C_6H_5 \cdot \text{CH} \cdot \text{CH}(\text{CH}_3) \\ | \\ C_6H_5 \cdot \text{CH} \cdot \text{CH}(\text{CH}_3) \end{array} > \text{CO},$$
 which, like the *cyclopentenone* from which it is formed, melts at  $122^\circ$ . In appearance, it is almost indistinguishable from the latter compound. It forms an *oxime* (m. p.  $165.5^\circ$ ) and a *dibromo-derivative*, 
$$\begin{array}{c} C_6H_5 \cdot \text{CH} \cdot \text{CBr}(\text{CH}_3) \\ | \\ C_6H_5 \cdot \text{CH} \cdot \text{CBr}(\text{CH}_3) \end{array} > \text{CO}$$
 (m. p.  $192^\circ$ , with decomposition).

This diphenyldimethyl*cyclopentanone* is more conveniently obtained by boiling  $\alpha\beta$ -dimethylanhydrazetonebenzil for some time with hydriodic acid and red phosphorus, the *cyclopentenone* which is first formed being thus further reduced.

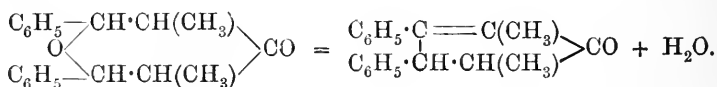
It may also be prepared in the same way from diphenyldimethyltetrahydro- $\gamma$ -pyrone.

Diphenyldimethyl*cyclopentenone* (m. p.  $122^\circ$ ) and diphenyldimethyl*cyclopentanone*, when dissolved together in equal quantities, form mixed crystals, perfectly homogeneous in appearance, melting at  $102$ — $103^\circ$ , and having a specific gravity which is almost exactly the mean of those of the two pure substances. Mixed crystals of a different melting point can, however, also be obtained, showing that their composition is not constant. We first obtained these mixed crystals in an experiment in which diphenyldimethyltetrahydro- $\gamma$ -pyrone was boiled for only a few minutes with hydriodic acid, and their formation under these circumstances shows that diphenyldimethyl*cyclopentenone* is the first product in the transformation of the  $\gamma$ -pyrone derivative into diphenyldimethyl*cyclopentanone* by hydriodic acid in the reaction just described.

Dibenzylideneacetone, when reduced with hydriodic acid, yielded only a gum from which nothing definite could be isolated. It behaves

in a totally different manner from the supposed dibenzylidenediethyl ketone.

In condensing benzaldehyde with diethyl ketone to obtain the diphenyldimethyltetrahydro- $\gamma$ -pyrone required for the present research, we employed a stronger solution of potassium hydroxide than is prescribed by Vorländer. We thus obtained, along with the expected  $\gamma$ -pyrone derivative, a compound formed from it by the removal of the elements of a molecule of water. This new compound, which melts at  $128^\circ$ , is readily prepared from diphenyldimethyltetrahydro- $\gamma$ -pyrone by leaving it in contact with alcoholic potassium hydroxide in the cold. It is 4:5-diphenyl-1:3-dimethylcyclopenten(5)-one(2), and is formed as follows:

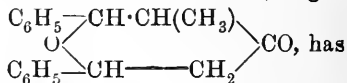


We shall give later on our reasons for assigning this constitution to the compound; but it may be noted here that diphenyldimethyltetrahydro- $\gamma$ -pyrone yields by dehydration two different diphenyldimethylcyclopentenones (that of m. p.  $122^\circ$  and that of m. p.  $128^\circ$ ) according as hydrogen chloride or potassium hydroxide is employed as a dehydrant.

The diphenyldimethylcyclopentenone melting at  $128^\circ$  is transformed, by warming it with alcohol to which a few drops of hydrochloric acid have been added, into the isomeride melting at  $122^\circ$ ; but an attempt to effect the reverse change by heating the latter compound with alcoholic potassium hydroxide gave only an amorphous product.

The present diphenyldimethylcyclopentenone (m. p.  $128^\circ$ ) yields an *oxime* (m. p.  $121.5^\circ$ ), a *dibromide*,  $\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{CBr} \cdot \text{CBr}(\text{CH}_3) \\ | \\ \text{C}_6\text{H}_5 \cdot \text{CH} - \text{CH}(\text{CH}_3) \end{array} \rangle \text{CO}$  (m. p.  $185^\circ$ , with decomposition), and, by reduction with hydriodic acid, is converted into diphenyldimethylcyclopentanone (m. p.  $122^\circ$ ) identical with the substance of that constitution already described.

A compound,  $\text{C}_{18}\text{H}_{18}\text{O}_2$ , which, from its modes of formation, might be diphenylmethyltetrahydro- $\gamma$ -pyrone,

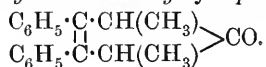


has been prepared by Levinstein (*Inaugural-Diss.*, Berlin, 1902) by the condensation of 2 mols. of benzaldehyde with 1 of methyl ethyl ketone under the influence of sodium hydroxide, and by Harries and Müller (*Ber.*, 1902, 35, 968) by condensing in a similar manner benzaldehyde with  $\alpha$ -benzylidenemethyl ethyl ketone. Levinstein found, as the melting point of the condensation compound,  $74^\circ$ ; Harries and Müller,  $68.5^\circ$ .

As it appeared possible that this compound might, like diphenyl-dimethyltetrahydro- $\gamma$ -pyrone, be converted, by treatment with hydrochloric acid, or hydriodic acid, or potassium hydroxide, into compounds containing a pentacarbon ring, we prepared it by the two foregoing methods. In both cases we obtained a mixture of two isomeric compounds of the empirical formula  $C_{18}H_{18}O_2$ , melting respectively at  $82-83^\circ$  and  $102-103^\circ$ . These could be separated by crystallisation, and we believe that the discrepant and much too low melting points observed by Levinstein, on the one hand, and Harries and Müller, on the other, are due to the fact that these investigators were dealing with mixtures of the two compounds. As both compounds are colourless, it is improbable that they are  $\alpha\gamma$ -dibenzylidene-methyl ethyl ketones. Possibly they are stereoisomeric diphenyl-methyltetrahydro- $\gamma$ -pyrones; but as they could not be converted into either of the known compounds of which we were in search—diphenyl-methylcyclopentenone and diphenylmethylcyclopentane—we did not investigate them further.

## EXPERIMENTAL.

## I. 4:5-Diphenyl-1:3-dimethylcyclopenten(4)-one(2),



Eight grams of finely-powdered  $\alpha\beta$ -dimethylanhydracetonebenzil,  $C_6H_5 \cdot \overset{\cdot}{C} = \overset{\cdot}{C}(CH_3) > CO$  (m. p.  $150^\circ$ ), were boiled for 5 minutes over a free flame with an excess of fuming hydriodic acid (sp. gr. 1.96). The product was precipitated with water and dissolved in ether; the ethereal solution was successively treated with solutions of sulphurous acid and sodium carbonate; and the neutral substance which remained after expelling the ether was purified by distillation under 12 mm. pressure and subsequent recrystallisation from alcohol, from which it was deposited in colourless scales, melting constantly at  $122^\circ$ .

Analysis gave figures agreeing with the formula of the expected diphenyldimethylcyclopentenone.

0.1599 gave 0.5086  $CO_2$  and 0.0987  $H_2O$ . C = 86.74; H = 6.85.

0.1552 „ 0.4919  $CO_2$  „ 0.0978  $H_2O$ . C = 86.44; H = 7.00.

$C_{19}H_{18}O$  requires C = 87.02; H = 6.87 per cent.

Different specimens were used for analysis.

By spontaneous evaporation from a solution in ethyl acetate with the addition of light petroleum, the substance is obtained in clear, prismatic crystals, showing an extinction angle of about  $34^\circ$  from the vertical axis, having a sp. gr. of 1.1775 at  $15^\circ$ , and melting as above

at 122°. Sometimes the prisms are flattened, causing them to assume a tabular habit.

Japp and Michie (Trans., 1903, 83, 303) prepared this compound for the purpose of comparing it with the substance of the same melting point and same composition which they had obtained by the reduction of diphenyldimethyltrihydroxycyclopentanone with hydriodic acid, and found that the two were identical.

As this diphenyldimethylcyclopentenone agreed also in properties and composition with the substance which Vorländer and Wilcke (Ber., 1898, 31, 1887) obtained by the action of hydrogen chloride on diphenyldimethyltetrahydro- $\gamma$ -pyrone and which they regard as dibenzylidenediethyl ketone, we prepared this supposed dibenzylidenediethyl ketone according to their method. No difference in physical properties between the substances obtained by the two methods could be detected. Both melted at 122°, and no depression of melting point was observed on mixing the two specimens.

As no case is known of the formation of an open-chain compound by the reduction of anhydracetonebenzil derivatives with hydriodic acid—as these substances, on the contrary, all yield, as first stage of the reduction, cyclopentenone derivatives containing the complex  $C_6H_5 \cdot \underset{|}{C} : \underset{|}{C} \cdot C_6H_5$ —we ascribe to Vorländer and Wilcke's supposed dibenzylidenediethyl ketone the cyclopentenone constitution already given.

The oxime (m. p. 157—159°) which they describe (*loc. cit.*) has therefore the constitution 
$$C_6H_5 \cdot \underset{|}{C} \cdot CH(CH_3) > C : N \cdot OH.$$

*Action of Bromine on Diphenyldimethylcyclopentenone* (m. p. 122°).—Vorländer and Wilcke (*loc. cit.*) assert that their "dibenzylidenediethyl ketone" forms an additive compound with 4 atoms of bromine. This observation, if correct, would form a very strong argument in favour of the constitution which they ascribe to this substance. We, therefore, repeated their experiment, adhering strictly to the conditions which they prescribe.

One and a half grams of diphenyldimethylcyclopentenone (m. p. 122°), prepared by Vorländer and Wilcke's method, were dissolved in chloroform, 4 grams of bromine were added, and the whole was left for 24 hours. Although the materials had been carefully dried, hydrogen bromide was evolved in the reaction. After expelling the solvent and the excess of bromine at the ordinary temperature by means of a current of dry air, and recrystallising the residue from benzene with the addition of methyl alcohol, the substance was obtained in small, oblique, four-sided plates, melting at about 180° with previous decomposition. This agrees with Vorländer and Wilcke's description.

0.2414 gave 0.3140 AgBr. Br = 55.35.

$C_{19}H_{16}OBr_4$  requires Br = 55.17 per cent.

Vorländer and Wilcke's analyses agree better with this formula than with that which they assign to the compound. The value for hydrogen is decisive. Thus, whilst  $C_{19}H_{16}OBr_4$  requires H = 2.76, Vorländer and Wilcke's formula,  $C_{19}H_{18}OBr_4$ , requires H = 3.09 per cent. They find H = 2.8 per cent. This value, together with the fact that hydrogen bromide is evolved in the formation of the substance, decides in favour of the formula  $C_{19}H_{16}OBr_4$ . The compound is formed by the addition of 2 atoms of bromine to diphenyldimethylcyclopentenone and the substitution of 2 further atoms of bromine for hydrogen in the resulting compound. The substance is therefore *diphenyldimethyl-tetrabromocyclopentanone*,  

$$\begin{array}{c} C_6H_5 \cdot CBr \cdot CBr(CH_3) \\ | \\ C_6H_5 \cdot CBr \cdot CBr(CH_3) \end{array} > CO.$$

*Action of Bromine on Diphenylcyclopentenone*,  

$$\begin{array}{c} C_6H_5 \cdot C \cdot CH_2 \\ || \\ C_6H_5 \cdot C \cdot CH_2 \end{array} > CO. —$$

The following experiment shows that diphenylcyclopentenone, the first product of the reduction of anhydracetonebenzil with hydriodic acid, behaves towards bromine like its dimethyl homologue.

Half a gram of diphenylcyclopentenone (m. p. 110°) was dissolved in chloroform and treated with 1.3 grams of bromine. Hydrogen bromide was evolved, and the solution, when left overnight, deposited reddish crystals. The mixture was left for 2 days and then treated as in the previous case. The crystalline residue was dissolved in alcohol, from which it was deposited in slender, colourless needles, which sinter and turn red at 120°, melting completely at about 130° (yield 0.4 gram).

0.1944 gave 0.2658 AgBr. Br = 58.19.

$C_{17}H_{12}OBr_4$  requires Br = 57.97 per cent.

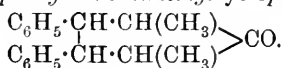
The compound is a *diphenyltetrabromocyclopentanone*, doubtless of the constitution  

$$\begin{array}{c} C_6H_5 \cdot CBr \cdot CHBr \\ | \\ C_6H_5 \cdot CBr \cdot CHBr \end{array} > CO.$$

It is readily decomposable, and in two subsequent attempts which we made to prepare it, in order to obtain material for a complete analysis, there was formed instead, probably by splitting off of hydrogen bromide from the tetrabromo-derivative, a compound melting at about 190—200°. This was not further examined.

We also tried the action of bromine under similar conditions on diphenylmethylcyclopentenone (compare Japp and Meldrum, Trans., 1901, 79, 1032), but as we failed to obtain the product in a crystallisable form, we did not examine it further.

## II. 4:5-Diphenyl-1:3-dimethylcyclopentanone(2),



Nine grams of  $\alpha\beta$ -dimethylanhydracetonebenzil, 18 grams of red phosphorus, and 135 grams of hydriodic acid (sp. gr. 1.7) were boiled together for  $1\frac{1}{2}$  hours. The resulting solid mass was separated from the excess of acid, pulverised, washed with water, and extracted with ether. The ethereal extract was successively shaken with solutions of sulphurous acid and sodium carbonate. On expelling the ether a crystalline mass remained, which was purified by recrystallisation, first from light petroleum (b. p. 50—80°) and afterwards from alcohol. The substance was thus obtained in colourless blades, melting constantly at 122°. The melting point thus coincides with that of the diphenyldimethylcyclopentenone already described, and the two substances are very similar in appearance; but a mixture of equal weights of the two was found to melt as low as 100—102°.

Analysis gave figures agreeing with the formula of a *diphenyldimethylcyclopentanone*.

0.1574 gave 0.4956 CO<sub>2</sub> and 0.1077 H<sub>2</sub>O. C = 85.87; H = 7.60.

0.1908 „ 0.6014 CO<sub>2</sub> „ 0.1304 H<sub>2</sub>O. C = 85.96; H = 7.59.

C<sub>19</sub>H<sub>20</sub>O requires C = 86.36; H = 7.58 per cent.

The foregoing experiment was made with the object of preparing the hydrocarbon, diphenyldimethylcyclopentane; as both anhydracetonebenzil and the two methylanhydracetonebenzils yield, when boiled with hydriodic acid and red phosphorus, the corresponding cyclopentanes; but in the present case the reduction appears not to proceed beyond the formation of the saturated cyclic ketone. The first stage of the reduction is, of course, the formation of diphenyldimethylcyclopentenone (m. p. 122°) as already described.

Diphenyldimethylcyclopentanone may be distilled under reduced pressure without decomposing.

By spontaneous evaporation of its solution in ethyl acetate, with the addition of light petroleum, it was obtained in six-sided, tabular crystals, showing straight extinction, having a sp. gr. of 1.1393 at 15°, and melting as above at 122°. Sometimes the crystals display a prismatic habit.

Happening to meet with (in an experiment to be described later on) certain crystals which behaved, on melting, like a mixture of diphenyldimethylcyclopentanone with the corresponding cyclopentenone melting at 122°, we made a mixture of equal weights of these two compounds, dissolved it in ethyl acetate, and added light petroleum. The solution

deposited irregular crystals, melting at 100—102°, and having a sp. gr. of 1.1546 at 15°. This specific gravity is almost exactly the mean of those of the two constituent substances: namely, 1.1393 for the *cyclopentanone*, and 1.1775 for the *cyclopentenone*. One crystal, however, did not melt until 108°, showing that the proportion of the constituents in the mixed crystals is not invariable.

*Reduction of Diphenyldimethylcyclopentenone* (m. p. 122°).—A specimen of diphenyldimethyl*cyclopentenone* (m. p. 122°), prepared by Vorländer and Wilcke's method (V. and W.'s "dibenzylidenediethyl ketone"), was boiled for 5 hours\* with hydriodic acid (sp. gr. 1.7) and red phosphorus. Purified by the process already described, it gave six-sided, tabular crystals of *diphenyldimethylcyclopentanone*, melting at 122°. The crystals were further identified by their optical properties and sp. gr., and by the mixture melting-point test, employing for admixture a specimen of diphenyldimethyl*cyclopentanone* prepared from  $\alpha\beta$ -dimethylanhydracetonebenzil. The mixture melted at 122°, whilst a mixture of the crystals with the unreduced diphenyldimethyl*cyclopentenone* (m. p. 122°) melted as low as 110°.

*Action of Hydriodic Acid on Diphenyldimethyltetrahydro- $\gamma$ -pyrone*.—Five grams of the finely-powdered  $\gamma$ -pyrone were boiled for 5 minutes with excess of fuming hydriodic acid (sp. gr. 1.96). The product, purified in the usual way, was obtained by crystallisation from ethyl acetate, with the addition of light petroleum, in six-sided, tabular crystals which, from their vague melting point—110—119°—sp. gr. 1.1695, and other properties were apparently mixed crystals of *diphenyldimethylcyclopentenone* and *diphenyldimethylcyclopentanone*, although, as the higher sp. gr. showed, containing a greater proportion of the former constituent than the mixed crystals already described. We were in fact able to prepare crystals of approximately the foregoing physical properties by allowing a mixture of 3 parts of diphenyldimethyl*cyclopentenone* (m. p. 122°) with 1 part of diphenyldimethyl*cyclopentanone* to crystallise from ethyl acetate with the addition of light petroleum. The separation of the constituents of such mixed crystals by crystallisation would be a very tedious process, if indeed it is at all feasible.

The reaction consists (1) in the transformation of the diphenyldimethyltetrahydro- $\gamma$ -pyrone into diphenyldimethyl*cyclopentenone* (m. p. 122°), the hydriodic acid playing the part of the hydrochloric acid in Vorländer and Wilcke's reaction (*loc. cit.*) for the preparation of the same compound; and (2) in the reduction of a portion of the *cyclopentenone* to a *cyclopentanone*, as in the reaction already

\* In the earlier experiments, we boiled the various substances with the reducing mixture for five hours, but we afterwards found that boiling for a shorter period (one and a half hours) gave a better yield.

described. That this explanation is correct, is shown by the fact that, by the more protracted action of boiling hydriodic acid on diphenyldimethyltetrahydro- $\gamma$ -pyrone, as described in the following experiment, only diphenyldimethylcyclopentanone is obtained.

Six grams of diphenyldimethyltetrahydro- $\gamma$ -pyrone, 12 grams of red phosphorus, and 90 grams of hydriodic acid (sp. gr. 1.7) were boiled together for 5 hours. The product, purified in the usual way, was found to consist of *diphenyldimethylcyclopentanone*. After recrystallising it twice from alcohol, 3 grams of this compound, melting constantly at  $122^{\circ}$ , were obtained. It was identified by the mixture melting-point test, and by the form, optical properties, and specific gravity of the crystals deposited by spontaneous evaporation from its solution in ethyl acetate with addition of light petroleum.

*Oxime of Diphenyldimethylcyclopentanone*.—Two grams of diphenyldimethylcyclopentanone, 1.5 grams of hydroxylamine hydrochloride, and a sufficiency of absolute alcohol, were introduced into a flask fitted with a reflux condenser, and the mixture was boiled for 4 hours on the water-bath, adding 1.6 grams of anhydrous sodium carbonate in small quantities at a time. The liquid was filtered while hot, and water was added to the filtrate until a turbidity was produced. The crystals, which were gradually deposited, were recrystallised from alcohol. The substance was thus obtained in two forms: slender needles and minute laminae. The melting point exhibits an anomaly: the substance generally melts at  $158-159^{\circ}$ , but after allowing it to cool and resolidify, does not melt until  $165.5^{\circ}$ . Sometimes crystals are obtained which show the higher melting point without previous fusion and resolidification; and these crystals induce the growth of their own kind in supersaturated solutions of the oxime. The substance is obviously dimorphous.

A nitrogen determination gave figures agreeing with the formula of the expected *oxime*.

0.2658 gave 11.4 c.c. moist nitrogen at  $12^{\circ}$  and 775 mm.  $N = 5.19$ .

$C_{19}H_{21}ON$  requires  $N = 5.02$  per cent.

In another preparation, this substance, possibly owing to local superheating, was obtained in brownish crystals, which had to be decolorised by boiling their alcoholic solution with animal charcoal.

*Action of Bromine on Diphenyldimethylcyclopentanone*.—1.4 grams of diphenyldimethylcyclopentanone were dissolved in chloroform, 4 grams of bromine, also dissolved in chloroform, were added, and the mixture was left for 24 hours. Hydrogen bromide was evolved, and on expelling the chloroform and excess of bromine in a current of dry air, small, tabular crystals were deposited. The substance crystallises from benzene, on addition of methyl alcohol, in radiating groups of

needles or prisms. It also crystallises from light petroleum in small prisms, and from ether in needles. The crystals show oblique extinction. Heated slowly, the crystals melt at  $179^\circ$ , turning red and decomposing; but by plunging the capillary tube containing the substance into a bath already heated to  $180^\circ$ , and raising the temperature rapidly, the melting point  $192^\circ$  (with decomposition) was observed. The yield was 2 grams.

0.2749 gave 0.5442  $\text{CO}_2$  and 0.1070  $\text{H}_2\text{O}$ .  $\text{C} = 53.99$ ;  $\text{H} = 4.32$ .

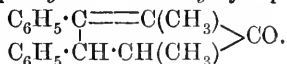
0.1783 „ 0.1593  $\text{AgBr}$ .  $\text{Br} = 38.02$ .

$\text{C}_{19}\text{H}_{18}\text{OBr}_2$  requires  $\text{C} = 54.03$ ;  $\text{H} = 4.27$ ;  $\text{Br} = 37.91$  per cent.

The compound is therefore a *diphenyldimethyldibromocyclopentanone*, doubtless of the constitution

$$\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{CH} \cdot \text{CBr}(\text{CH}_3) \\ | \\ \text{C}_6\text{H}_5 \cdot \text{CH} \cdot \text{CBr}(\text{CH}_3) \end{array} > \text{CO}.$$

III. 4 : 5-*Diphenyl-1 : 3-dimethylcyclopenten(5)-one(2)*,



In preparing the diphenyldimethyltetrahydro- $\gamma$ -pyrone used in the foregoing experiments, we had no very precise details of the method previously used to guide us. Vorländer and Hobohm (*Ber.*, 1896, 29, 1352), who first prepared this compound, merely mention that it is obtained by the condensation of 2 mols. of benzaldehyde with 1 mol. of diethyl ketone in presence of alcohol and aqueous potassium hydroxide. On the other hand, the method described by Vorländer (*Annalen*, 1896, 294, 296) for condensing these two substances is intended primarily to yield benzylidenediethyl ketone, the  $\gamma$ -pyrone derivative being obtained only as a by-product. We gather, however, from the description there given, that, in the experiment about to be described, we probably used a considerably stronger solution of potassium hydroxide than was employed by Vorländer and Hobohm—a circumstance which doubtless accounts for our obtaining, along with the  $\gamma$ -pyrone derivative, a substance not observed by our predecessors in this work.

One hundred and twenty grams of benzaldehyde, 40 grams of diethyl ketone, 300 c.c. of absolute alcohol, 250 c.c. of water, and 10 c.c. of a 33.3 per cent. solution of potassium hydroxide were mixed in a stout bottle; the mixture, which was clear at first, speedily became turbid and in a short time separated into two layers, indicating the occurrence of the first stage of the condensation. Fifty grams of solid potassium hydroxide were then added in successive portions of 10 grams each, shaking after each addition, until everything had gone into solution, before adding the next portion. The whole was then

mechanically shaken until the organic substance had become quite pasty, which required about  $4\frac{1}{2}$  days. The product was separated by filtration, pressed, and dissolved in boiling methyl alcohol. As the solution cooled, prismatic crystals of diphenyldimethyltetrahydro- $\gamma$ -pyrone\* separated. The mother liquor was decanted from these while the solution was still warm, in order to prevent a second substance, melting at  $128^\circ$ , which, as we had ascertained from a previous experiment, is formed at the same time, from crystallising out. The yield of almost pure  $\gamma$ -pyrone derivative thus obtained was 41 grams, and more was separated from the mother liquor. The decanted solution, on further cooling, deposited a second substance crystallising in large, serrated blades, mixed, however, with diphenyldimethyltetrahydro- $\gamma$ -pyrone. The new compound was purified by fractional crystallisation from methyl alcohol or ethyl alcohol, in which it is much less soluble than the  $\gamma$ -pyrone derivative. It melted, as already stated, at  $128^\circ$ . It is formed in relatively small quantity, which accounts for its remaining, in spite of its more sparing solubility, in the first mother liquor.

0.1661 gave 0.5276  $\text{CO}_2$  and 0.1034  $\text{H}_2\text{O}$ .  $\text{C} = 86.62$ ;  $\text{H} = 6.91$ .

0.1766 „ 0.5626  $\text{CO}_2$  „ 0.1094  $\text{H}_2\text{O}$ .  $\text{C} = 86.88$ ;  $\text{H} = 6.88$ .

$\text{C}_{19}\text{H}_{18}\text{O}$  requires  $\text{C} = 87.02$ ;  $\text{H} = 6.87$  per cent.

The reactions of this compound show that it is 4:5-diphenyl-1:3-dimethylcyclopenten(5)-one(2), as formulated at the head of the present section of this paper.

A portion of the compound was distilled under a pressure of 12 mm. The distillate consisted of a small quantity of needle-shaped crystals embedded in a vitreous matrix. On crystallising from alcohol, needles were obtained (m. p. about  $257^\circ$ ) in quantity too small for further examination. The greater portion of the distillate was an uncrystallisable gum.

The compound, therefore, decomposes when distilled. For this reason Vorländer and Hobohm would not have been able to detect the presence of this substance, even had it been formed in their reaction, as they purified their crude diphenyldimethyltetrahydro- $\gamma$ -pyrone by distillation.

*Transformation of Diphenyldimethyltetrahydro- $\gamma$ -pyrone into 4:5-Diphenyl-1:3-dimethylcyclopenten(5)-one(2).*—Our suspicion that the formation of the diphenyldimethylcyclopentenone melting at  $128^\circ$  was due to the

\* The melting point of diphenyldimethyltetrahydro- $\gamma$ -pyrone is given by Vorländer and Hobohm (*loc. cit.*) at  $106^\circ$ . M. M. Richter ("Lexikon") gives, in addition, the melting point  $109^\circ$ , the authority for which we have not been able to trace. We find that the substance, when sufficiently purified by recrystallisation from methyl alcohol, melts constantly at  $111.5$ — $112.5^\circ$ .

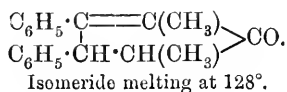
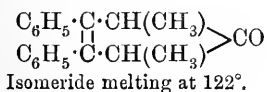
action of the relatively strong solution of potassium hydroxide on diphenyldimethyltetrahydro- $\gamma$ -pyrone primarily formed, was confirmed by the following experiment, in which, by using a still stronger solution of alkali, the transformation is complete.

To a solution of 75 grams of potassium hydroxide in 300 grams of absolute alcohol, 24 grams of the finely-powdered pyrone were added, and the mixture was mechanically shaken for a week, after which it was left for another week, shaking it from time to time. The appearance of the undissolved substance had totally changed: the liquid was filled with glistening laminae. The product, separated by filtration, weighed 10.5 grams. By recrystallisation from boiling alcohol, it was separated into two substances: pink-coloured laminae melting at  $128^\circ$ , and needles melting at  $265^\circ$ , the latter compound being obtained in quantity too small for further examination. By recrystallisation from methyl alcohol, the plates were obtained colourless and melted as before at  $128^\circ$ . The substance was identical with the 4:5-diphenyl-1:3-dimethylcyclopenten(5)-one(2) just described, as was proved by the mixture melting-point test.

We also examined the action of strong alcoholic potassium hydroxide in the cold on diphenyltetrahydro- $\gamma$ -pyrone (previously prepared by Petrenko-Kritschenko and Plotnikoff, *Ber.*, 1897, 30, 2802), in the hope of obtaining a diphenylcyclopentenone isomeric with that which is formed by the reduction of anhydracetonebenzil; but as the product of the reaction was amorphous, we did not further investigate it.

*Behaviour of the Isomeric Diphenyldimethylcyclopentenones towards Potassium Permanganate.*—Alcoholic solutions of the two diphenyldimethylcyclopentenones (m. p.  $122^\circ$  and m. p.  $128^\circ$ ) were prepared, a few drops of sodium carbonate solution were added to each, and then a drop of a solution of potassium permanganate. In the case of the compound melting at  $122^\circ$ , the mixture required 15 minutes to turn brown; with the isomeride melting at  $128^\circ$ , the change occurred immediately.

This difference in behaviour indicates, in the first place, that the two compounds differ in their structure, and are not merely stereoisomeric. There are only two formulæ possible for structurally isomeric diphenyldimethylcyclopentenones containing the methyl and phenyl groups in the positions in which they are present in these compounds; and we would assign these as follows to the two compounds:



The first formula explains the greater stability of the compound

towards permanganate, inasmuch as compounds containing the group  $\text{C}_6\text{H}_5 \cdot \underset{\text{I}}{\underset{|}{\text{C}}} \cdot \text{C}_6\text{H}_5$ , in which no hydrogen is attached to the ethylene complex, are specially stable towards permanganate; thus, diphenylmaleic acid dissolved in sodium carbonate does not reduce permanganate in the cold. This first formula, moreover, is in keeping, as has been already mentioned, with the formation of the compound by the reduction of  $\alpha\beta$ -dimethylanhydracetonebenzil with hydriodic acid. These formulæ also account for the behaviour of the respective compounds with bromine and towards reducing agents.

*Oxime of 4:5-Diphenyl-1:3-dimethylcyclopenten(5)-one(2).* — The diphenyldimethylcyclopentenone melting at  $128^\circ$  was converted into its oxime by the process already described in the case of the corresponding cyclopentanone. The product was purified by recrystallisation, first from ethyl alcohol, then from methyl alcohol, and finally from light petroleum. It was thus obtained in short, flat needles, which soften at  $115^\circ$  and melt at  $121.5^\circ$ .

A nitrogen determination gave a value agreeing with that required for the expected *oxime*.

0.2245 gave 10.05 c.c. moist nitrogen at  $11^\circ$  and 757 mm.  $\text{N} = 5.31$ .

$\text{C}_{19}\text{H}_{19}\text{ON}$  requires  $\text{N} = 5.05$  per cent.

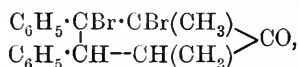
*Action of Bromine on 4:5-Diphenyl-1:3-dimethylcyclopenten(5)-one(2).* — One gram of the diphenyldimethylcyclopentenone melting at  $128^\circ$  was dissolved in chloroform, and to the cold solution 2.5 grams of bromine, also dissolved in chloroform, were added. Heat was evolved, but no hydrogen bromide was given off. The mixture was left for 24 hours, after which the solvent and the excess of bromine were expelled in a current of dry air. The resulting crystalline product weighed 1.8 grams. It was recrystallised once from ethyl alcohol and twice from benzene with the addition of methyl alcohol. It was deposited from the latter solvent in radiating groups of prisms or needles melting at  $185^\circ$  with decomposition. The best crystals were obtained from light petroleum. They showed straight extinction.

0.2940 gave 0.5820  $\text{CO}_2$  and 0.1144  $\text{H}_2\text{O}$ .  $\text{C} = 53.99$ ;  $\text{H} = 4.32$ .

0.2212 „ 0.1973 AgBr.  $\text{Br} = 37.96$ .

$\text{C}_{19}\text{H}_{18}\text{OBr}_2$  requires  $\text{C} = 54.03$ ;  $\text{H} = 4.27$ ;  $\text{Br} = 37.91$  per cent.

The compound is therefore the additive *dibromide*,



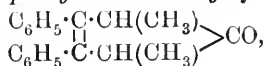
and the addition of bromine is not accompanied by substitution as it is in the case of the isomeric diphenyldimethylcyclopentanone melting at  $122^\circ$ . It is isomeric with the compound obtained by bromina-

ting diphenyldimethylcyclopentanone. The melting points of the two compounds are too indefinite and too close together to serve as a criterion, and the crystalline forms are very similar; but the optical properties of the two kinds of crystals (*v. supra*) distinguish sharply between them.

*Action of Hydriodic Acid.*—One gram of the diphenyldimethylcyclopentenone melting at  $128^\circ$ , 2 grams of red phosphorus, and 15 grams of hydriodic acid (sp. gr. 1.7) were boiled for 4 hours. The product, purified in the usual way, was deposited from alcohol in elongated plates melting at  $122^\circ$ . The specific gravity, the form, and the optical properties of the crystals were those of *diphenyldimethylcyclopentanone*, and the identity of the compound was established by the mixture melting-point test. On the other hand, when the substance was mixed with a specimen of the diphenyldimethylcyclopentenone melting at  $122^\circ$ , the melting point was considerably depressed.

The result of the foregoing reduction shows that the compound melting at  $128^\circ$  contains the cyclopentenone group.

*Action of Alcoholic Hydrochloric Acid.*—Half a gram of the diphenyldimethylcyclopentenone melting at  $128^\circ$  was dissolved in absolute alcohol, 20 drops of a saturated alcoholic solution of hydrochloric acid were added, and the whole was heated on the water-bath for 1 hour. The solution, which had become concentrated, deposited, on cooling, needle-shaped crystals of a substance melting at about  $260^\circ$ , the quantity of which was too small for further examination. The mother liquor, when further evaporated, yielded six-sided plates of a substance, which, after recrystallisation from alcohol and subsequently from ethyl acetate, with addition of light petroleum, was obtained in the characteristic forms of 4:5-diphenyl-1:3-dimethylcyclopenten(4)-one(2),



with an extinction angle of  $34^\circ$  and melting at  $122^\circ$ . The mixture melting-point test, in which we employed for admixture a specimen of this compound prepared by the reduction of  $\alpha\beta$ -dimethylanhydracetonebenzil, gave no depression.

Under the influence of hydrochloric acid, therefore, the position of the double bonds is shifted from the 1:5- to the 4:5-position, and the diphenyldimethylcyclopentenone melting at  $128^\circ$  is transformed into its isomeride melting at  $122^\circ$ .

It is possible therefore that, in the reduction of the diphenyldimethylcyclopentenone (m. p.  $128^\circ$ ) with hydriodic acid and red phosphorus, the foregoing transformation, occurring under the influence of the acid, precedes the reduction.

IV. *Two Isomeric Compounds of the Formula  $C_{18}H_{18}O_2$ , obtained by the Condensation of Benzaldehyde with Methyl Ethyl Ketone.*

We determined to prepare diphenylmethyltetrahydro- $\gamma$ -pyrone in order to ascertain whether it could be converted into compounds containing the pentacarbon ring. Two methods were available for the preparation of this substance: that of Levinstein (*Inaugural-Diss.*, Berlin, 1902) and that of Harries and Müller (*Ber.*, 1902, 35, 968).

Levinstein obtained the compound by the condensation of benzaldehyde with methyl ethyl ketone under the influence of sodium hydroxide. We carried out the process as follows, and as our results differ from those of our predecessors, we will describe the procedure in detail.

One hundred and twenty grams of benzaldehyde, 33 grams of methyl ethyl ketone, 200 c.c. of alcohol, 480 c.c. of water, and 33 grams of a 10 per cent. aqueous solution of sodium hydroxide were mixed, and the mixture was mechanically shaken for a week. The pasty mass of organic substance was dissolved in ether and, after drying the ethereal solution with calcium chloride, the ether was expelled and the residue distilled under about 12 mm. pressure. The following fractions were collected:

1. Up to  $140^\circ$ . Mainly benzaldehyde.
2.  $140-200^\circ$ . Solidified almost immediately, and consisted chiefly of  $\alpha$ -benzylidenemethyl ethyl ketone.
3.  $200-250^\circ$ . Viscid oil.

Fraction 3 was redistilled, and the chief sub-fraction, which passed over between  $220^\circ$  and  $240^\circ$  (12 mm. pressure), was dissolved in boiling methyl alcohol. A crop of crystals weighing 15.5 grams was obtained, but the substance was evidently a mixture. It was redissolved in boiling light petroleum (b. p.  $80-100^\circ$ ), which deposited it in two forms: plates, and tufts of needles. By mechanical separation and recrystallisation of the separated products from methyl alcohol, the two compounds were obtained in sufficient quantity to serve as nuclei in the subsequent process of fractional crystallisation. The remainder of the mixture was dissolved in boiling light petroleum, and the crystallisation was started with one of the substances, separating the crop by filtration before the solution was cold. The crystallisation of the filtrate, after previous concentration, was started with the second substance. Finally, the separated substances were recrystallised from methyl alcohol until they showed constant melting points. We thus obtained (1) large six-sided plates melting at  $82-83^\circ$ ; (2) long rectangular plates melting at  $102-103^\circ$ . Both compounds gave, on analysis, figures agreeing with the formula  $C_{18}H_{18}O_2$ .

*Compound melting at 82—83°.*

0.1100 gave 0.5359  $\text{CO}_2$  and 0.1804  $\text{H}_2\text{O}$ .  $\text{C} = 81.02$ ;  $\text{H} = 6.75$ .

$\text{C}_{18}\text{H}_{18}\text{O}_2$  requires  $\text{C} = 81.23$ ;  $\text{H} = 6.77$  per cent.

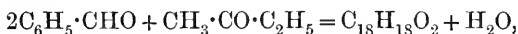
*Compound melting at 102—103°.*

0.1731 gave 0.5157  $\text{CO}_2$  and 0.1071  $\text{H}_2\text{O}$ .  $\text{C} = 81.25$ ;  $\text{H} = 6.87$ .

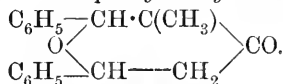
0.1878 „ 0.5622  $\text{CO}_2$  „ 0.1148  $\text{H}_2\text{O}$ .  $\text{C} = 81.64$ ;  $\text{H} = 6.79$ .

$\text{C}_{18}\text{H}_{18}\text{O}_2$  requires  $\text{C} = 81.23$ ;  $\text{H} = 6.77$  per cent.

The compounds are formed according to the equation



and might be stereoisomeric *diphenylmethyltetrahydro- $\gamma$ -pyrones*,



We also employed Harries and Müller's method of preparation (*loc. cit.*) by shaking a mixture of  $\alpha$ -benzylidenemethyl ethyl ketone and benzaldehyde with an aqueous-alcoholic solution of sodium hydroxide, but obtained the same two compounds melting respectively at 82—83° and 102—103°. This experiment disposes of the possible objection that one or both of these compounds might have been formed from an impurity in the methyl ethyl ketone which we employed.

Levinstein gives the melting point of his condensation compound  $\text{C}_{18}\text{H}_{18}\text{O}_2$  as 74°; Harries and Müller give 68.5° for theirs. As already mentioned, we suspect that these investigators were dealing with mixtures of the two compounds just described.

We studied the action of hot alcoholic hydrogen chloride on both these compounds, and of hydriodic acid at its boiling point, and of alcoholic potassium hydroxide in the cold, on the compound melting at 102—103°, but did not succeed in isolating anything definite from the products of the reactions.

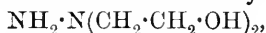
CHEMICAL DEPARTMENT,  
UNIVERSITY OF ABERDEEN.

CXLIX.—*Interaction of Sodium Phenylglycidate with Phenylhydrazine.*

By FRANCIS ROBERT JAPP, F.R.S., and WILLIAM MAITLAND, B.Sc.,  
Carnegie Fellow in the University of Aberdeen.

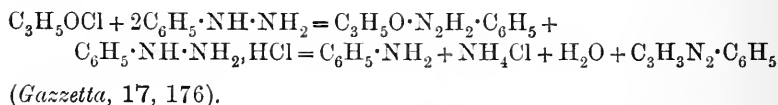
THE action of hydrazines on compounds containing the ethylene oxide group ("αβ-oxido-compounds"—compare Japp and Michie, *Trans.*, 1903, 83, 281, footnote) has been relatively little studied.

By the action of hydrazine on ethylene oxide, Knorr and Brownsdon (*Ber.*, 1902, 35, 4474) obtained *as*-diethanolhydrazine,

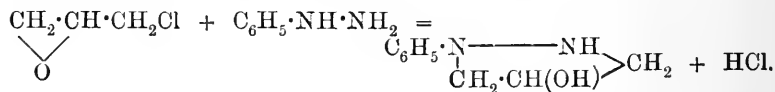


which, by dehydration, yielded a small quantity of morpholylhydrazine along with a considerable amount of morpholine.

A more complex case had been previously studied by Balbiano in the action of epichlorhydrin on hydrazines. By heating epichlorhydrin with twice its molecular proportion of phenylhydrazine, a mixture of 1-phenylpyrazole, aniline and ammonium chloride was obtained :



The intermediate compound  $\text{C}_9\text{H}_{12}\text{ON}_2$ , the formation of which was assumed by Balbiano, was obtained by F. Gerhard (*Ber.*, 1891, 24, 352) by the interaction of epichlorhydrin and phenylhydrazine at the ordinary temperature. He explains its formation as follows :



Such a compound would be 1-phenyl-4-hydroxytetrahydropyrazole. It yields a monacetyl derivative and, when heated with phenylhydrazine hydrochloride, is converted into 1-phenylpyrazole as in Balbiano's second equation.

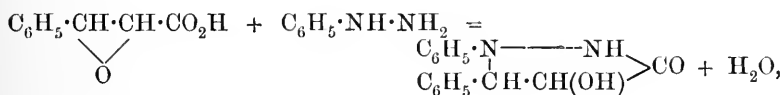
Japp and Michie (*Trans.*, 1903, 83, 283, 284 and 286) showed that both acetodiphenylmethyloxidobutyric acid and diphenyldimethyloxidoglutaric acid give, with phenylhydrazine, reactions somewhat similar to the foregoing, the oxido-group of the acid interacting additively with the basic imino-group of the phenylhydrazine, and the resulting compound parting with water to form, in the case of the first acid, a pyrazolidone ring and, in that of the second, both a pyrazolidone and a furfuran ring (compare *loc. cit.*).

Owing to the complexity of the compounds formed in these two cases, it seemed desirable to study the reaction with an oxido-compound of a simpler character, and in this way to prepare, if possible, some substance of already known constitution, so as to test the validity of the interpretation put upon the reaction by Japp and Michie. We selected for this purpose phenylglycidic acid ( $\beta$ -phenyl- $\alpha\beta$ -oxido-propionic acid), which, on account of the instability of the free acid, we employed in the form of its sodium salt. The reaction was further of interest because Erlenmeyer, jun. (*Annalen*, 1892, 271, 167), in comparing the reactions of phenylpyruvic acid with those of the isomeric phenylglycidic acid, shows that the former compound interacts with phenylhydrazine, but he apparently takes for granted that phenylglycidic acid will not do so. Had he tried the experiment he would have found that both acids interact with phenylhydrazine according to the equation :

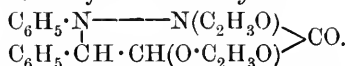


the resulting compounds, however, being quite distinct.

We find, therefore, that when phenylglycidic acid, in the form of its sodium salt, is heated with phenylhydrazine in alcoholic solution, these substances interact, yielding 1:5-diphenyl-4-hydroxy-3-pyrazolidone,

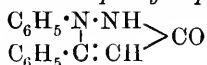


this compound being obtained in the form of its sodium salt, which, when recrystallised from water, has the formula  $\text{C}_{15}\text{H}_{13}\text{O}_2\text{N}_2\text{Na}\cdot 4\text{H}_2\text{O}$ . The pyrazolidone, liberated by acids, dissolves in sodium carbonate, regenerating this salt. It yields a *diacetyl* derivative,

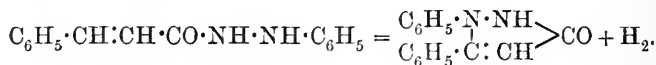


By heating the sodium salt of the pyrazolidone with methyl iodide, the *methyl* derivative,  $\begin{array}{c} \text{C}_6\text{H}_5\cdot\text{N} \text{---} \text{N}(\text{CH}_3) \\ | \qquad \qquad | \\ \text{C}_6\text{H}_5\cdot\text{CH}\cdot\text{CH}(\text{OH}) \end{array} > \text{CO}$ , is obtained, which has no acid properties, is not hydrolysed by sodium hydroxide, and yields a *monacetyl* derivative.

By distilling the pyrazolidone under reduced pressure, or, better, by fusing it with zinc chloride, or by warming it for some hours with a solution of potassium hydroxide or sodium carbonate, it parts with water and is converted into 1:5-diphenyl-3-pyrazolone,



(m. p. 252°), previously obtained by Knorr (*Ber.*, 1887, 20, 1107) by distilling *cinnamoylphenylhydrazine*:



This diphenylpyrazolone yields a *monacetyl* derivative.

The compound which we have formulated as a diphenylhydroxypyrazolidone is not reduced by sodium in boiling alcoholic solution, is not oxidised by Fehling's solution, and does not interact with benzaldehyde even at the boiling point of the latter substance. These negative results, taken in conjunction with the facts that the compound forms a diacetyl derivative and also a methyl derivative which is insoluble in and not hydrolysable by alkalis, exclude the constitutional formula  $\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C} : \text{CH} \cdot \text{CO}_2\text{H} \\ \text{N}(\text{C}_6\text{H}_5) \cdot \text{NH}_2 \end{array}$ , which might otherwise call for consideration.

We found that sodium phenylglycidate also interacted with hydrazine hydrate and with  $\beta$ -naphthylhydrazine, but as we were unable to obtain the products in a crystallised condition, we did not investigate them further.

#### EXPERIMENTAL.

*Action of Phenylhydrazine on Sodium Phenylglycidate: Formation of 1:5-Diphenyl-4-hydroxy-3-pyrazolidone.*—Ten grams of sodium phenylglycidate, 10 grams of phenylhydrazine and 50 c.c. of alcohol were introduced into a tube, which was then exhausted, sealed up, and heated for 9 hours at 100° in a water-bath. During the earlier part of the heating, the tube was shaken from time to time, until the whole of the sodium phenylglycidate had dissolved. On allowing the contents of the tube to cool and diluting with alcohol, a crystalline sodium salt separated, the amount of which increased on standing. This was filtered off, washed with cold alcohol, ground with ether, again filtered, and washed with ether. The yield of salt, thus treated, was 13 grams. On dissolving a portion of this salt in water and acidifying with dilute sulphuric acid, an organic substance was precipitated. The organic compound crystallised from alcohol in rectangular laminae, and from benzene in needles, melting at 173·5°.

0·1553 gave 0·4021 CO<sub>2</sub> and 0·0813 H<sub>2</sub>O. C=70·61; H=5·82.

0·1624 „ 15·0 c.c. moist nitrogen at 10° and 755 mm. N=10·99.

C<sub>15</sub>H<sub>14</sub>O<sub>2</sub>N<sub>2</sub> requires C=70·86; H=5·51; N=11·02 per cent.

This is the composition of 1:5-diphenyl-4-hydroxy-3-pyrazolidone,

$$\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{N} \text{---} \text{NH} \\ | \\ \text{C}_6\text{H}_5 \cdot \text{CH} \cdot \text{CH}(\text{OH}) \end{array} > \text{CO},$$
 a constitution to which the reactions of this substance point.

A portion of the foregoing sodium salt was recrystallised twice from water, from which it was deposited in indistinct needle-shaped crystals. It became pink-coloured in the process. Analysis gave figures agreeing with the formula  $\text{C}_{15}\text{H}_{13}\text{O}_2\text{N}_2\text{Na}, 4\text{H}_2\text{O}$ .

0.4050 lost, at  $80^\circ$ , 0.0822.  $\text{H}_2\text{O} = 20.30$ .

$\text{C}_{15}\text{H}_{13}\text{O}_2\text{N}_2\text{Na}, 4\text{H}_2\text{O}$  requires  $\text{H}_2\text{O} = 20.69$  per cent.

0.3228 anhydrous salt gave 0.0828  $\text{Na}_2\text{SO}_4$ .  $\text{Na} = 8.31$ .

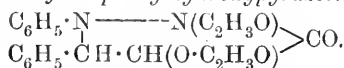
$\text{C}_{15}\text{H}_{13}\text{O}_2\text{N}_2\text{Na}$  requires  $\text{Na} = 8.33$  per cent.

The weight of the salt dried at  $80^\circ$  is practically constant. A very little above that temperature the substance begins to decompose. The salt crystallises from hot alcohol in tufts of needles.

The pyrazolidone dissolves in a hot solution of sodium carbonate. On cooling, the liquid deposits the foregoing salt. The heating with the sodium carbonate solution should not be continued longer than is necessary to dissolve the substance, otherwise dehydration of the product occurs, and 1:5-diphenyl-3-pyrazolone is formed (*v. infra*).

The pyrazolidone can be titrated, although not quite accurately, with sodium hydroxide in alcoholic solution, using phenolphthalein as an indicator. Thus 1 gram of the pyrazolidone required 0.1549 gram  $\text{NaOH}$  for neutralisation; the calculated value being 0.1575 gram  $\text{NaOH}$ , on the assumption that  $\text{C}_{15}\text{H}_{14}\text{O}_2\text{N}_2$  behaves like a monobasic acid.

*Diacetyl Derivative of Diphenylhydroxypyrazolidone,*



—The pyrazolidone was boiled with 10 times its weight of acetic anhydride for  $6\frac{1}{2}$  hours, the excess of anhydride was distilled off under reduced pressure, and the residue was recrystallised from alcohol. It formed short needles, melting constantly at  $152^\circ$ .

0.1516 gave 0.3726  $\text{CO}_2$  and 0.0746  $\text{H}_2\text{O}$ .  $\text{C} = 67.03$ ;  $\text{H} = 5.47$ .

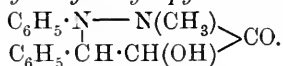
0.1757 „ 12.5 c.c. moist nitrogen at  $12^\circ$  and 761 mm.  $\text{N} = 8.45$ .

$\text{C}_{19}\text{H}_{18}\text{O}_4\text{N}_2$  requires  $\text{C} = 67.45$ ;  $\text{H} = 5.33$ ;  $\text{N} = 8.28$  per cent.

When the diacetyl derivative is digested on the water-bath with a solution of sodium carbonate, it dissolves very slowly. In the process it is hydrolysed, but the resulting diphenylhydroxypyrazolidone is dehydrated by the long digestion, yielding 1:5-diphenyl-3-pyrazolone (*v. infra*). This substance was precipitated by acidifying with acetic acid. It crystallised from alcohol in needles melting at  $252^\circ$ , and was further identified by the mixture melting-point test.

Warming for some time with dilute alcoholic sodium hydroxide produces the same change.

1:5-Diphenyl-2-methyl-4-hydroxy-3-pyrazolidone,



—A quantity of the sodium salt of diphenylhydroxypyrazolidone was boiled with a slight excess of methyl iodide in methyl-alcoholic solution for  $3\frac{1}{2}$  hours. On pouring the product into water an oil separated, which soon solidified. A further quantity of the same substance was obtained by extracting the aqueous-alcoholic mother liquor with ether. By washing the product with a little ether and recrystallising from hot alcohol, the substance was obtained in six-sided crystals, sometimes elongated, or even lath-shaped, melting at  $163\text{--}164^\circ$ . It is slightly soluble in water.

0.1860 gave 0.4861  $\text{CO}_2$  and 0.1015  $\text{H}_2\text{O}$ .  $\text{C} = 71.27$ ;  $\text{H} = 6.06$ .

0.1533 „ 13.55 c.c. moist nitrogen at  $10^\circ$  and 756.5 mm.  $\text{N} = 10.54$ .

$\text{C}_{16}\text{H}_{16}\text{O}_2\text{N}_2$  requires  $\text{C} = 71.64$ ;  $\text{H} = 5.97$ ;  $\text{N} = 10.45$  per cent.

The substance is thus a *methyl* derivative of diphenylhydroxypyrazolidone.

As it appeared to be slightly more soluble in aqueous sodium hydroxide than in water, we were at first inclined to credit it with acid properties. A titration experiment, however, showed that it does not interact with the alkali. A small quantity of the substance (0.3272 gram) was dissolved in alcohol with phenolphthalein as an indicator, and 0.2 c.c. of an alcoholic solution of sodium hydroxide (4.87 NaOH per litre) was added. The lavender coloration which phenolphthalein gives with alkaline hydroxides in strong alcohol was at once produced, and did not disappear either on standing or on warming. The methyl derivative, therefore, unlike the parent substance, cannot be titrated under the foregoing conditions, nor is it hydrolysed by the alkali. These results indicate that the methyl group is attached to nitrogen and not to oxygen, and that the compound is therefore 1:5-diphenyl-2-methyl-4-hydroxy-3-pyrazolidone.

By protracted warming with aqueous sodium hydroxide on the water-bath, the compound was totally decomposed.

Attempts to dehydrate the methyl derivative to a diphenylmethylpyrazolone, either by distilling it under reduced pressure or by heating it with zinc chloride—methods, which, as will be seen later on, gave positive results in the case of diphenylhydroxypyrazolidone—were unavailing. In both cases only unchanged substance was recovered.

*Acetyl Derivative*,  $\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{N} - \text{N}(\text{CH}_3) \\ | \\ \text{C}_6\text{H}_5 \cdot \text{CH} \cdot \text{CH}(\text{O} \cdot \text{C}_2\text{H}_3\text{O}) \end{array} > \text{CO}$ .—The methyl derivative was acetylated with acetic anhydride, as described in the case

of the pyrazolidone, boiling for 3 hours. The product crystallised from alcohol in obliquely-terminated, flat prisms, or in oblique plates with bevelled edges, melting at  $155^{\circ}$ . Analysis showed that a *mon-acetyl* derivative had been formed.

0.1556 gave 0.3946  $\text{CO}_2$  and 0.0831  $\text{H}_2\text{O}$ .  $\text{C} = 69.16$  ;  $\text{H} = 5.93$ .

0.1695 „ 13.6 c.c. moist nitrogen at  $18^{\circ}$  and 759.5 mm.  $\text{N} = 9.26$ .

$\text{C}_{18}\text{H}_{18}\text{O}_3\text{N}_2$  requires  $\text{C} = 69.68$  ;  $\text{H} = 5.81$  ;  $\text{N} = 9.03$  per cent.

*Dehydration of 1:5-Diphenyl-4-hydroxy-3-pyrazolidone: Formation of 1:5-Diphenyl-3-pyrazolone,*  $\text{C}_6\text{H}_5\cdot\text{N}\cdot\text{NH}\cdot\text{C}(\text{C}_6\text{H}_5)=\text{CH}\cdot\text{CO}$  (m. p.  $252^{\circ}$ ).—One gram of diphenylhydroxypyrazolidone was heated in an Anschütz flask (a distilling flask with the receiver fused on to the tubulure) which was kept exhausted during the process by means of a Sprengel mercury pump. A reaction took place when the temperature of the oil-bath reached  $230^{\circ}$ , and the temperature was ultimately raised to  $285^{\circ}$ . Needle-shaped crystals condensed in the neck of the flask; these were twice recrystallised from glacial acetic acid, after which they melted constantly at  $252^{\circ}$ , and were found to be 1:5-diphenyl-3-pyrazolone formed by abstraction of the elements of 1 mol. of water from diphenylhydroxypyrazolidone. For comparison a specimen of the compound was prepared by Knorr's method (*Ber.*, 1887, 20, 1107) of distilling cinnamoylphenylhydrazine. The two specimens were indistinguishable from one another; both melted at  $252^{\circ}$ , and there was no depression of melting point on mixing the two. A nitrogen determination confirmed this result.

0.1207 gave 12.0 c.c. moist nitrogen at  $13^{\circ}$  and 763 mm.  $\text{N} = 11.79$ .

$\text{C}_{15}\text{H}_{12}\text{ON}_2$  requires  $\text{N} = 11.86$  per cent.

Gas was given off in the foregoing reaction, a resinous mass remained behind in the flask, and the yield of purified diphenylpyrazolone was only one-fifth of the weight of substance taken.

We afterwards discovered various other means of dehydrating diphenylhydroxypyrazolidone which gave much better yields of diphenylpyrazolone.

Thus diphenylhydroxypyrazolidone was mixed with solid zinc chloride and a few drops of water, and the mixture heated in a test-tube until the water was driven off and a clear yellow fused mass was produced. On dissolving the cooled mass in hot alcohol to which a few drops of acetic acid had been added, a solution was obtained which, on cooling, deposited an excellent yield of the diphenylpyrazolone (m. p.  $252^{\circ}$ ).

Also by dissolving diphenylhydroxypyrazolidone in 8 per cent. aqueous potassium hydroxide, or even in sodium carbonate solution,

and heating on the water-bath at 100° for 2—4 hours, a solution is obtained which, on acidifying, gives diphenylpyrazolone. The yield is again good.

In an experiment in which we tried to reduce diphenylhydroxypyrazolidone by heating it on the water-bath with tin and aqueous-alcoholic hydrochloric acid, it was found that the compound had merely been dehydrated, yielding the foregoing diphenylpyrazolone.

As, by these various reactions, we had come into possession of a few grams of 1:5-diphenyl-3-pyrazolone, we studied some of the reactions of this substance. It is soluble in aqueous potassium hydroxide and is precipitated from the solution by carbon dioxide. An attempt to titrate the pyrazole in alcoholic solution with alcoholic sodium hydroxide, using phenolphthalein as an indicator, gave, however, a very unsatisfactory result, as only about three-quarters of the theoretical amount of sodium hydroxide was neutralised by the pyrazole, assuming that the latter acts as a monobasic acid.

2-Acetyl-1:5-diphenyl-3-pyrazole,  $\begin{matrix} \text{C}_6\text{H}_5 \cdot \text{N} \cdot \text{N}(\text{C}_2\text{H}_5\text{O}) \\ | \\ \text{C}_6\text{H}_5 \cdot \text{C} = \text{CH} \end{matrix} > \text{CO}.$ —Diphenylpyrazole (m. p. 252°) was boiled for 4 hours with 10 times its weight of acetic anhydride. On distilling off the excess of anhydride under reduced pressure, a gum was left; on dissolving this in light petroleum, the solution, by spontaneous evaporation, deposited four-sided prisms, or thick, rhombic plates, melting constantly at 65—66°. A nitrogen determination showed that a *monacetyl* derivative had been formed.

0.1489 gave 12.8 c.c. moist nitrogen at 19° and 772 mm. N = 10.0.

$\text{C}_{17}\text{H}_{14}\text{O}_2\text{N}_2$  requires N = 10.07 per cent.

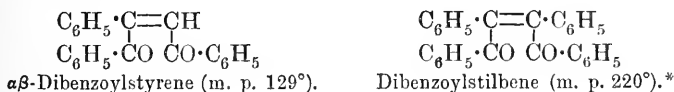
CHEMICAL DEPARTMENT,  
UNIVERSITY OF ABERDEEN.

### CL.—*a*-Benzoyl- $\beta$ -trimethacetylstyrene.

By FRANCIS ROBERT JAPP, F.R.S., and WILLIAM MAITLAND, B.Sc.,  
Carnegie Fellow in the University of Aberdeen.

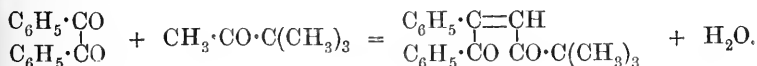
JAPP and KLINGEMANN (Trans., 1890, 57, 662) studied the peculiar transformations which  $\alpha\beta$ -dibenzoylstyrene ( *$\alpha\beta$ -dibenzoylcinnamene*—compare Trans., 1901, 79, 1013, footnote) undergoes under the influence of heat and of various chemical agents—transformations frequently involving the migration of a phenyl group. They were,

moreover, able to show that these reactions were in almost every instance analogous to those of Zinin's "acicular oxylepiden" (dibenzoylstilbene), and in this way they succeeded in clearing up the constitution of the majority of the derivatives prepared by the latter investigator from this substance. The relation of the two compounds to one another is shown by the formulæ



It seemed of interest to prepare some further representative of this class of unsaturated  $\gamma$ -diketones in order to ascertain whether it would exhibit similar reactions.

$\alpha\beta$ -Dibenzoylstyrene is obtained by the condensation of benzil with acetophenone under the influence of potassium hydroxide. By substituting methyl *tert.*-butyl ketone for acetophenone in this reaction, we were able to prepare  $\alpha$ -benzoyl- $\beta$ -trimethacetylstyrene (m. p.  $115^\circ$ ) according to the equation,

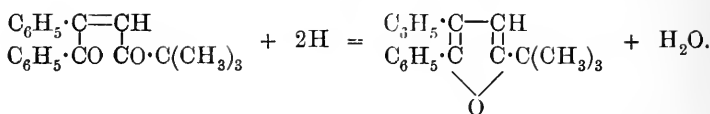


In order that an unsaturated  $\gamma$ -diketone may with certainty be formed by the condensation of benzil with a ketone, it is necessary that one of the radicles of the ketone should be a primary alkyl and the other either a tertiary alkyl or an aryl. Unless this second condition is fulfilled, a closed-chain compound—a derivative of anhydrazetone benzil—will generally result. Thus benzil and methyl *isopropyl* ketone yield  $\beta\beta$ -dimethylanhydrazetonebenzil,  $\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C}=\text{CH} \\ | \quad | \\ \text{C}_6\text{H}_5 \cdot \text{C}(\text{OH}) \cdot \text{C}(\text{CH}_3)_2 \end{array} > \text{CO}$  (Japp and Meldrum, *Trans.*, 1901, 79, 1037).

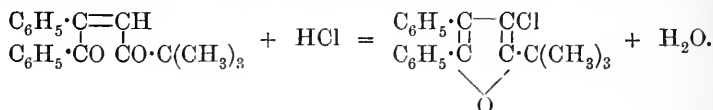
As the reactions of benzoyltrimethacetylstyrene for the most part run parallel with those of dibenzoylstyrene and dibenzoylstilbene, we will not, in the individual cases, call further attention to this parallelism, but will restrict ourselves to indicating where the reactions deviate in character from those previously described. The parallel reactions of dibenzoylstyrene and dibenzoylstilbene are given in the paper by Japp and Klingemann already quoted.

Benzoyltrimethacetylstyrene is readily converted into furfuran derivatives. Thus by boiling it with hydriodic acid it is reduced to 4:5-diphenyl-2-*tert.*-butylfurfuran (m. p.  $68-69.5^\circ$ ):

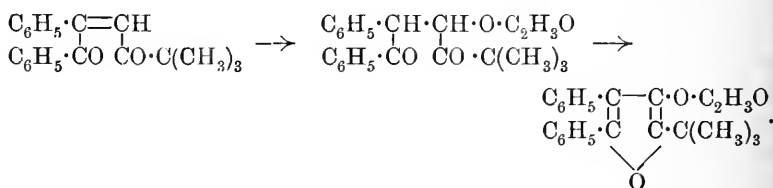
\* Both of these compounds, as will be shown in a paper to be published shortly by one of us in conjunction with Mr. James Wood, have the *cis*-configuration.



It interacts with hydrogen chloride in alcoholic solution to form 3-chloro-4:5-diphenyl-2-tert.-butylfurfuran (m. p. 87—88°):



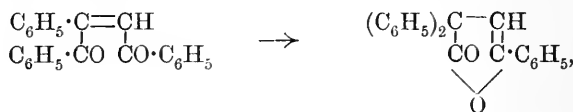
In like manner it interacts with acetic anhydride to which a few drops of concentrated sulphuric acid have been added, yielding 3-acetoxy-4:5-diphenyl-2-tert.-butylfurfuran (m. p. 99—100°). In this case the reaction consists in an addition of acetic acid to the unsaturated  $\gamma$ -diketone, followed by elimination of water:



The corresponding reaction in the case of dibenzoylstyrene was discovered by J. Thiele (*Ber.*, 1898, 31, 1248). The mechanism of Thiele's reaction is the same as in the formation of chlorotriphenylfurfuran from dibenzoylstyrene and hydrogen chloride (Japp and Klingemann, *loc. cit.*, p. 663).

The two last-mentioned reactions cannot occur in the case of dibenzoylstilbene, as in this compound there is no hydrogen directly attached to the ethylene group.

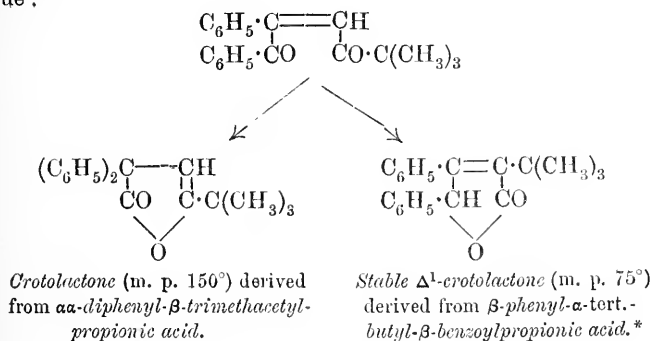
Japp and Klingemann (*loc. cit.*, p. 665) showed that when dibenzoylstyrene is heated, it is for the most part converted into the isomeric triphenylcrotonolactone (m. p. 117—118°):



a small quantity of the isomeric *trans*-dibenzoylstyrene being formed at the same time.

The action of heat on  $\alpha$ -benzoyl- $\beta$ -trimethacetylstyrene differs from the foregoing inasmuch as *two* isomeric crotonolactones are formed, according as the necessary migration of a monad hydrocarbon radicle

occurs in the benzil residue or in the methyl *tert.*-butyl ketone residue :

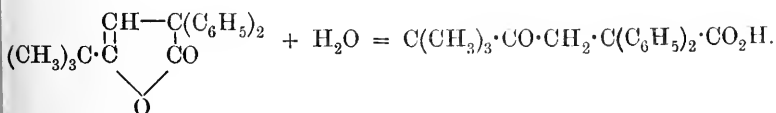


whilst no formation of the isomeric *trans*-benzoyltrimethacetylstyrene was observed.

Dibenzoylstyrene might of course yield two isomeric crotonlactones corresponding with the foregoing, according as the migration of a phenyl group occurred in the benzil residue or in the acetophenone residue; but only that formed according to the first of these processes was observed. Dibenzoylstilbene, on the other hand, with its symmetrical molecule, can yield only one crotonlactone—tetraphenylcrotonlactone, Zinin's so-called "tabular oxylepiden."

On oxidising the foregoing crotonlactone melting at  $150^\circ$  with chromium trioxide, *benzophenone* was obtained, thus proving that a phenyl group had migrated in the formation of the crotonlactone.

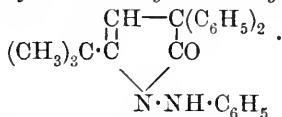
By the action of potassium hydroxide this crotonlactone was hydrolysed to *αα*-diphenyl- $\beta$ -trimethacetylpropionic acid (m. p.  $133\text{--}134^\circ$ ) :



This acid interacts with phenylhydrazine, eliminating 2 mols. of water and yielding a compound,  $\text{C}_{26}\text{H}_{26}\text{ON}_2$  (m. p.  $143\text{--}145^\circ$ ). Following the analogy of the compound formed in the corresponding reaction of *αα*-diphenyl- $\beta$ -benzoylpropionic acid with phenylhydrazine (Japp and Klingemann, *loc. cit.*, p. 665), this substance would be 1-phenyl-

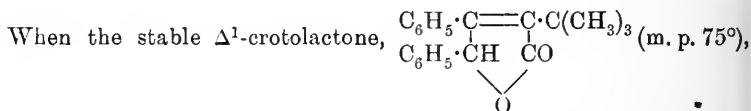
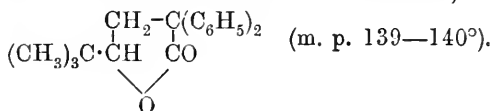
\* The corresponding *labile*  $\Delta^2$ -crotonlactone, derived from the same ketonic acid, is described later on. The reasons for assigning respectively the  $\Delta^1$ -unsaturated and  $\Delta^2$ -unsaturated constitution to these crotonlactones are to be found in J. Thiele's paper: "Ueber isomere Diphenylcrotonlactone" (*Annalen*, 1899, 306, 194).

*amino-2-keto-3 : 3-diphenyl-5-tert.-butyl-2 : 3-dihydropyrrhole,*



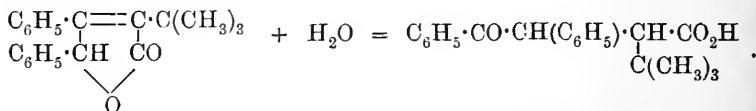
When diphenyltrimethacetylpropionic acid is heated, or when it is allowed to remain at the ordinary temperature with acetic anhydride to which a few drops of concentrated sulphuric acid have been added, it is reconverted into the *crotonolactone* melting at  $150^\circ$ .

By treating diphenyltrimethacetylpropionic acid in boiling alcoholic solution with sodium, it is reduced to *aa-diphenyl-γ-tert.-butyl-γ-hydroxybutyric acid*,  $\text{C}(\text{CH}_3)_3\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{C}(\text{C}_6\text{H}_5)_2\cdot\text{CO}_2\text{H}$ , which, when liberated from the sodium salt, forms the *butyrolactone*,

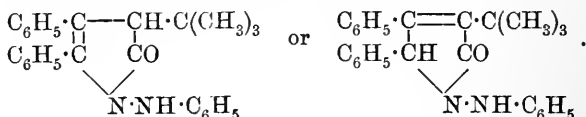


is oxidised with chromium trioxide, it yields *benzil*, along with a crystalline product melting at  $165-166^\circ$ , the latter being obtained in quantity too small for identification. The formation of benzil shows that no migration of a phenyl group has occurred in the production of this lactone from benzoyltrimethacetylstyrene.

By the action of potassium hydroxide the  $\Delta^1$ -crotonolactone (m. p.  $75^\circ$ ) is hydrolysed to *β-phenyl-α-tert.-butyl-β-benzoylpropionic acid* (m. p.  $183-184^\circ$ ):



This acid (m. p.  $183-184^\circ$ ) interacts with phenylhydrazine, eliminating 2 mols. of water and yielding a compound,  $\text{C}_{26}\text{H}_{26}\text{ON}_2$  (m. p.  $185-186^\circ$ ), which, on the analogy already referred to, might be either



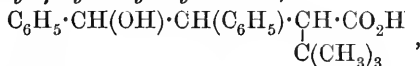
By the action of heat, *β-phenyl-α-tert.-butyl-β-benzoylpropionic acid* is dehydrated, regenerating the foregoing stable  $\Delta^1$ -crotonolactone (m. p.  $75^\circ$ ).

As this  $\gamma$ -ketonic acid has a hydrogen atom in the  $\alpha$ -position, it ought to be convertible, by treatment at the ordinary temperature with acetic anhydride to which a few drops of concentrated sulphuric acid have been added, into a labile  $\Delta^2$ -crotonolactone (compare J. Thiele, *Annalen*, 1899, 306, 196). This was found to be the case, and the

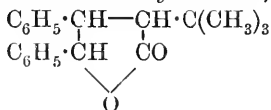
labile  $\Delta^2$ -crotonolactone,  $\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C} - \text{CH} \cdot \text{C}(\text{CH}_3)_3 \\ | \quad | \\ \text{C}_6\text{H}_5 \cdot \text{C} \quad \text{CO} \\ \diagdown \quad \diagup \\ \text{O} \end{array}$  (m. p. 119°), was after-

wards transformed, by boiling with acetic anhydride, into the *stable*  $\Delta^1$ -croto lactone (m. p. 75°) already mentioned—a transformation described by Thiele in the case of other labile  $\Delta^2$ -croto lactones.

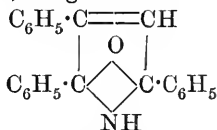
$\beta$ -Phenyl- $\alpha$ -tert.-butyl- $\beta$ -benzoylpropionic acid, when treated in boiling alcoholic solution with metallic sodium, is reduced to  $\beta\gamma$ -diphenyl- $\alpha$ -tert.-butyl- $\gamma$ -hydroxybutyric acid,



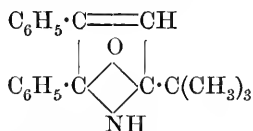
which, when liberated from the sodium salt, spontaneously eliminates water, and is transformed into its *butyrolactone*,

(m. p.  $155.5^{\circ}$ ).

Benzoyltrimethacetylstyrene interacts with ammonia, eliminating water and yielding an *imide* (m. p. 152°) having the formula  $C_{20}H_{21}ON$ . Japp and Tingle, on the ground that the corresponding imide of dibenzoylstyrene yielded, on reduction, 2 : 4 : 5-triphenylpyrrhole and, by oxidation, dibenzamide, assigned to it the constitution



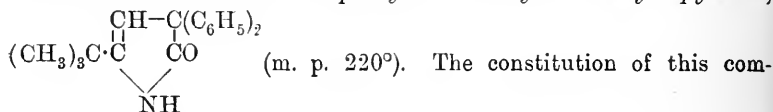
(Trans., 1897, 71, 1140). If the analogy of this compound is to be followed, the present imide would have the constitution



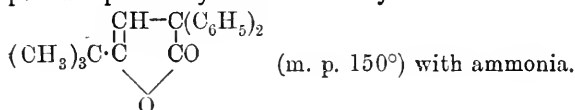
and might be termed 4 : 5-diphenyl-2-tert.-butyl-2 : 5-oxidopyrrole.\*

\* Regarding the use of the term "oxido" to indicate "bridge-oxygen," compare Japp and Michie (Trans., 1903, **83**, 281, footnote). M. Busch, on the other hand (*J. pr. Chem.*, 1903, [ii], **67**, 203), employs the prefix "endo" to denote a mobile

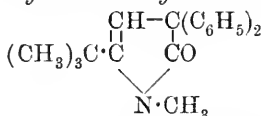
When this imide is heated above its melting point, it is converted into the isomeric 2-*keto*-3:3-diphenyl-5-*tert*.-butyl-2:3-dihydropyrrhole,



pound is proved by its formation by the interaction of the crotolactone



By the action of methylamine on benzoyltrimethacetylstyrene, 2-*keto*-3:3-diphenyl-1-methyl-5-*tert*.-butyl-2:3-dihydropyrrhole,

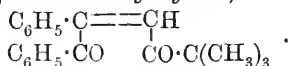


(m. p.  $112^\circ$ , not sharp), is produced. No intermediate compound corresponding with the imide is here formed.

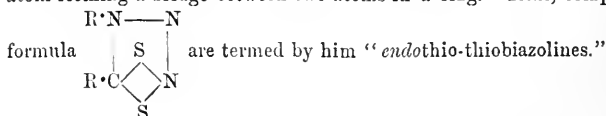
#### EXPERIMENTAL.

##### I. Preparation of $\alpha$ -Benzoyl- $\beta$ -trimethacetylstyrene (m. p. $115^\circ$ ).

Eighty grams of benzil, 48 grams of methyl *tert*.-butyl ketone, and 240 grams of absolute alcohol were warmed in a flask until the whole of the benzil had dissolved, after which the flask was rapidly cooled with water, shaking all the time so as to prevent the formation of large crystals of benzil. Sixteen grams of potassium hydroxide, dissolved in 24 grams of water, were then added, and the mixture was left in the corked flask for a fortnight, shaking from time to time. The benzil gradually disappeared, whilst another crystalline substance was gradually deposited in its place. The crystalline deposit was separated by filtration, washed with water to remove a little potassium benzoate, and recrystallised twice from boiling alcohol. It was thus obtained in pointed prisms melting at  $115^\circ$ . By spontaneous evaporation of its alcoholic solution it is obtained in rhombs showing the same melting point. Analysis gave figures agreeing with the formula of  $\alpha$ -benzoyl- $\beta$ -trimethacetylstyrene,



atom forming a bridge between two atoms in a ring. Thus, compounds having the



0.1925 gave 0.5768 CO<sub>2</sub> and 0.1196 H<sub>2</sub>O. C = 81.72; H = 6.90.

0.1498 „ 0.4496 CO<sub>2</sub> „ 0.0928 H<sub>2</sub>O. C = 81.85; H = 6.89.

C<sub>20</sub>H<sub>20</sub>O<sub>2</sub> requires C = 82.19; H = 6.85 per cent.

The yield of once crystallised and practically pure substance was 71 grams, whilst more could be obtained from the mother liquor.

In extracting with alcohol the crude product which had previously been washed with water, a substance was obtained which was almost insoluble in alcohol. It was recrystallised from benzene, but different preparations gave discrepant melting points, varying between 160—163° and 177°, and did not give concordant figures on analysis. The quantity was too small for further examination.

An attempt to obtain a condensation compound of 1 mol. of benzil with 2 mols. of methyl *tert.*-butyl ketone, using an alcoholic solution of sodium ethoxide as a condensing agent, as in J. Wislicenus and A. Lehmann's method of preparing dibenzoyldiphenylbutadiene from benzil and acetophenone (*Annalen*, 1898, 302, 198), yielded only impure benzoyltrimethacetylstyrene.

## II. Conversion of *α*-Benzoyl-*β*-trimethacetylstyrene into Furfuran Derivatives.

*Action of Hydriodic Acid on Benzoyltrimethacetylstyrene: Formation*

of 4 : 5-Diphenyl-2-*tert.*-butylfurfuran,

$$\begin{array}{c}
 \text{C}_6\text{H}_5 \cdot \text{C} \quad \text{CH} \\
 \parallel \quad \parallel \\
 \text{C}_6\text{H}_5 \cdot \text{C} \quad \text{C} \cdot \text{C}(\text{CH}_3)_3 \\
 \diagdown \quad \diagup \\
 \text{O}
 \end{array}
 \quad (\text{m. p.}$$

68—69.5°).—Three grams of finely-powdered benzoyltrimethacetylstyrene were boiled with fuming hydriodic acid (sp. gr. 1.96) for 5 minutes. The product was dissolved in ether, shaken successively with solutions of sulphurous acid and sodium carbonate, and the substance which remained after expelling the ether was distilled under 12 mm. pressure. The distillate, which passed over at 196—199°, weighed 2.3 grams; it was crystallised from methyl alcohol, from which it was deposited in four-sided, oblique plates, melting at 68—69.5°.

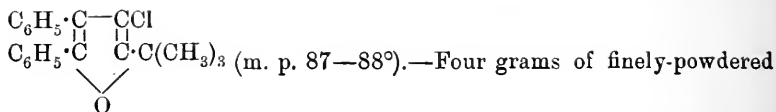
0.1616 gave 0.5125 CO<sub>2</sub> and 0.1044 H<sub>2</sub>O. C = 86.49; H = 7.17.

0.1569 „ 0.4987 CO<sub>2</sub> „ 0.1023 H<sub>2</sub>O. C = 86.68; H = 7.24.

C<sub>20</sub>H<sub>20</sub>O requires C = 86.95; H = 7.24 per cent.

From dilute acetic acid the compound crystallises in aggregates of large, oblique laminae, containing solvent of crystallisation.

*Action of Alcoholic Hydrogen Chloride on Benzoyltrimethacetylstyrene: Formation of 3-Chloro-4 : 5-diphenyl-2-tert.-butylfurfuran,*

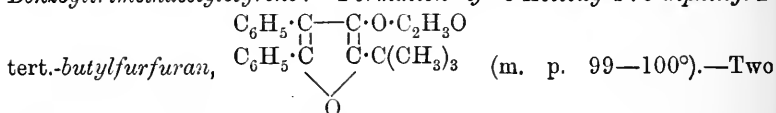


benzoyltrimethacetylstyrene were added to an excess of saturated alcoholic hydrogen chloride. The substance dissolved slowly in the cold, and the solution darkened slightly. In a few hours an oily product separated, which afterwards solidified. By recrystallisation from alcohol it was obtained in aggregates of long, slender, radiating needles, melting constantly at  $87-88^\circ$ .

0.4844 gave 0.2231 AgCl.  $\text{Cl} = 11.40$ .

$\text{C}_{20}\text{H}_{19}\text{OCl}$  requires  $\text{Cl} = 11.46$  per cent.

*Action of a Mixture of Acetic Anhydride and Sulphuric Acid on Benzoyltrimethacetylstyrene: Formation of 3-Acetoxy-4:5-diphenyl-2-*



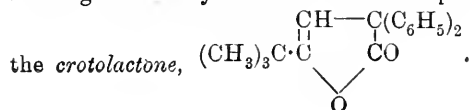
grams of benzoyltrimethacetylstyrene were dissolved in the cold in 10 c.c. of acetic anhydride to which 4 drops of concentrated sulphuric acid had been added, and the mixture was left for a day. The solution, which became reddish-coloured on mixing, deposited a solid substance; this was separated by filtration and purified by recrystallisation from boiling alcohol. It was thus obtained in short, lustrous, white needles which turned yellow on exposure to light; they melted at  $99-100^\circ$ . The substance dissolves in concentrated sulphuric acid, giving a solution with a faint green fluorescence (compare *Ber.*, 1898, 31, 1249).

0.1677 gave 0.4850  $\text{CO}_2$  and 0.0998  $\text{H}_2\text{O}$ .  $\text{C} = 78.87$ ;  $\text{H} = 6.61$ .

$\text{C}_{22}\text{H}_{22}\text{O}_3$  requires  $\text{C} = 78.74$ ;  $\text{H} = 6.59$  per cent.

### III. Action of Heat on $\alpha$ -Benzoyl- $\beta$ -trimethacetylstyrene.

Ten grams of benzoyltrimethacetylstyrene were heated for half an hour in a test-tube jacketed with diphenylamine vapour ( $310^\circ$ ). Some gas was given off during the process, and the fused substance turned brown, whilst needles of a new compound melting at  $150^\circ$  condensed in the cooler parts of the tube. The resulting brown mass, dissolved in benzene, gave, on addition of light petroleum, slender needles melting constantly at  $150^\circ$ . This compound, as its reactions show, is

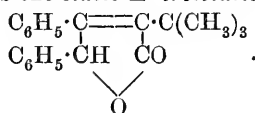


0.1506 gave 0.4548  $\text{CO}_2$  and 0.0965  $\text{H}_2\text{O}$ .  $\text{C} = 82.36$ ;  $\text{H} = 7.11$ .

0.1595 „ 0.4803  $\text{CO}_2$  „ 0.1002  $\text{H}_2\text{O}$ .  $\text{C} = 82.12$ ;  $\text{H} = 6.98$ .

$\text{C}_{20}\text{H}_{20}\text{O}_2$  requires  $\text{C} = 82.19$ ;  $\text{H} = 6.85$  per cent.

The mother liquor from the foregoing compound deposited thin plates, embedded in a yellow oil. By distilling this entire residue under reduced pressure, and recrystallising the distillate from alcohol, the substance was obtained in thin plates melting at  $75^\circ$ . Its reactions show that it is the *stable*  $\Delta^1$ -croto lactone,



0.1807 gave 0.5444  $\text{CO}_2$  and 0.1129  $\text{H}_2\text{O}$ .  $\text{C} = 82.17$ ;  $\text{H} = 6.94$ .

$\text{C}_{20}\text{H}_{20}\text{O}_2$  requires  $\text{C} = 82.19$ ;  $\text{H} = 6.85$  per cent.

In a preparation on a larger scale in which 71 grams of benzoyl-trimethacetylstyrene were heated in four portions and the products worked up together the yields were: compound (m. p.  $150^\circ$ ), 22 grams; compound (m. p.  $75^\circ$ ), 15 grams.

In one experiment a substance was obtained melting at about  $212^\circ$ , only sparingly soluble in the ordinary organic solvents although dissolving in solvent naphtha. The quantity was insufficient for further examination.

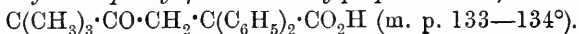
IV. *Croto lactone*,  $(\text{CH}_3)_3\text{C} \cdot \text{C} \begin{array}{l} \text{CH} - \text{C}(\text{C}_6\text{H}_5)_2 \\ | \quad \quad | \\ \text{CO} \end{array}$  (m. p.  $150^\circ$ ), *derived from*

*aa-Diphenyl- $\beta$ -trimethacetylpropionic Acid*,

$\text{C}(\text{CH}_3)_3 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{C}(\text{C}_6\text{H}_5)_2 \cdot \text{CO}_2\text{H}$  (m. p.  $133$ — $134^\circ$ ).

*Oxidation of Croto lactone* (m. p.  $150^\circ$ ).—1.5 grams of the croto lactone (m. p.  $150^\circ$ ) were dissolved in glacial acetic acid on the water bath, and an excess of chromium trioxide was gradually added, afterwards continuing the heating for a quarter of an hour. Water was then added and the oil which separated was extracted with ether. The ethereal solution was shaken with a solution of sodium carbonate, after which the ether was expelled and the residue distilled under reduced pressure. The distillate, which passed over when the oil-bath was at  $185^\circ$  (12 mm. pressure) was slightly coloured; it smelt like benzophenone and solidified on touching it with a fragment of this substance. After spreading it on a porous tile to absorb oil, it melted at  $46$ — $48.5^\circ$ . Mixed with a specimen of benzophenone (m. p.  $48$ — $49^\circ$ ) it melted at  $48$ — $49^\circ$ . It was therefore *benzophenone*.

*Action of Potassium Hydroxide on the Croto lactone* (m. p. 150°):  
*Formation of aa-Diphenyl-β-trimethacetylpropionic Acid*,



—A quantity of the croto lactone (m. p. 150°) was dissolved in alcoholic potassium hydroxide, and the mixture was evaporated to dryness on the water-bath. On dissolving the residue in water and acidifying, an oil was precipitated: this solidified to a hard mass. The substance, which was the ketonic acid sought for, was purified by recrystallisation from benzene with addition of light petroleum. It formed four-sided, oblique plates, with bevelled edges, and melted at 133—134°.

0.2038 gave 0.5774  $\text{CO}_2$  and 0.1336  $\text{H}_2\text{O}$ .  $\text{C} = 77.27$ ;  $\text{H} = 7.28$ .

$\text{C}_{20}\text{H}_{22}\text{O}_3$  requires  $\text{C} = 77.42$ ;  $\text{H} = 7.10$  per cent.

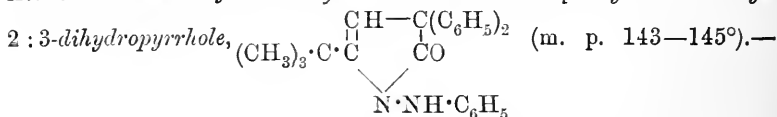
The *silver salt* was obtained as a white powder by precipitating a solution of the acid in ammonia with silver nitrate.

0.2416 gave 0.0640 Ag.  $\text{Ag} = 26.50$ .

$\text{C}_{20}\text{H}_{21}\text{O}_3\text{Ag}$  requires  $\text{Ag} = 25.90$  per cent.

The croto lactone (m. p. 150°) was also transformed into the foregoing *aa-diphenyl-β-trimethacetylpropionic acid* (m. p. 133—134°) by boiling it for 4 minutes with fuming hydriodic acid (sp. gr. 1.9). An acid melting at 145—147° was formed at the same time, but the quantity was insufficient for further study.

*Action of Phenylhydrazine on aa-Diphenyl-β-trimethacetylpropionic Acid: Formation of 1-Phenylamino-2-keto-3:3-diphenyl-5-tert.-butyl-*



Two grams of *aa-diphenyl-β-trimethacetylpropionic acid* (m. p. 133—134°) and 1.1 grams of phenylhydrazine, with a little absolute alcohol, were heated in a sealed tube at 150° for 1½ hours. On allowing the tube to remain for 24 hours in the cold a crystalline substance was deposited; this was purified by recrystallisation from alcohol, from which it separated in leaflets melting at 143—145°.

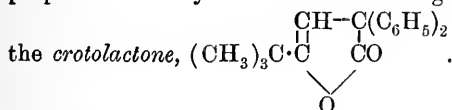
0.1648 gave 0.4937  $\text{CO}_2$  and 0.1020  $\text{H}_2\text{O}$ .  $\text{C} = 81.70$ ;  $\text{H} = 6.88$ .

0.2278 „ 14.90 c.c. moist nitrogen at 18° and 767 mm.  $\text{N} = 7.63$ .

$\text{C}_{26}\text{H}_{26}\text{ON}_2$  requires  $\text{C} = 81.67$ ;  $\text{H} = 6.81$ ;  $\text{N} = 7.33$  per cent.

*Action of Heat on aa-Diphenyl-β-trimethacetylpropionic Acid: Regeneration of the Croto lactone* (m. p. 150°).—Half a gram of the acid was heated in a test-tube jacketed with diphenylamine vapour (310°), until bubbles (aqueous vapour) ceased to be given off. The product, which was somewhat dark-coloured, was purified by recrystallisation

from benzene, with the addition of light petroleum. It was thus obtained in slender needles melting at  $150^\circ$ , which, by their physical properties and by the mixture melting-point test, were identified as



*Action of Acetic Anhydride containing a little Sulphuric Acid on  $\alpha\alpha$ -Diphenyl- $\beta$ -trimethacetylpropionic Acid.*—This reaction gave the same result as the foregoing. Eight c.c. of acetic anhydride were poured over 1 gram of  $\alpha\alpha$ -diphenyl- $\beta$ -trimethacetylpropionic acid. On adding 1 drop of concentrated sulphuric acid, the organic acid immediately dissolved. On adding a second drop, a substance crystallised out. Water was added, and the precipitated substance was recrystallised from alcohol. By its physical properties and by the mixture melting-point test, it was identified as the foregoing *crotolactone* (m. p.  $150^\circ$ ).

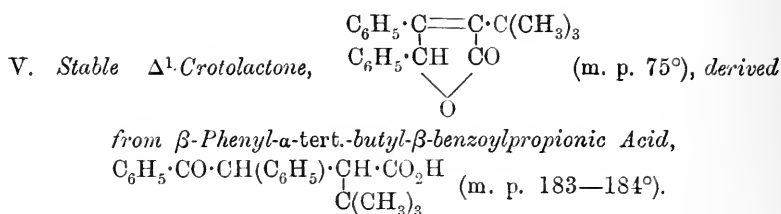
It should be noted that, in the case of the isomeric ketonic acid, to be described later on, two different *crotolactones* are obtained, according as the dehydration is effected by heating, or by the action of a mixture of acetic anhydride and sulphuric acid.

*Reduction of  $\alpha\alpha$ -Diphenyl- $\beta$ -trimethacetylpropionic Acid: Formation of the Lactone,*  $(\text{CH}_3)_3\text{C}\cdot\overset{\text{CH}_2}{\underset{\text{O}}{\text{C}}}-\overset{\text{CH}}{\underset{\text{CO}}{\text{C}}}(\text{C}_6\text{H}_5)_2$  (m. p.  $139$ — $140^\circ$ ), *of  $\alpha\alpha$ -Di-*

*phenyl- $\gamma$ -tert.-butyl- $\gamma$ -hydroxybutyric Acid.*—2.8 grams of  $\alpha\alpha$ -diphenyl- $\beta$ -trimethacetylpropionic acid (m. p.  $133$ — $134^\circ$ ) were dissolved in absolute alcohol, and 4 grams of sodium were gradually added to the boiling solution. The liquid was diluted with water and acidified, and the precipitated substance was purified by repeated crystallisation from alcohol. It formed slender needles melting at  $139$ — $140^\circ$ . Analysis showed that the hydroxy-acid, formed by reduction, had parted with water, yielding the foregoing *butyrolactone*.

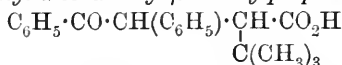
0.1574 gave 0.4713  $\text{CO}_2$  and 0.1054  $\text{H}_2\text{O}$ . C = 81.66; H = 7.44.

$\text{C}_{20}\text{H}_{22}\text{O}_2$  requires C = 81.63; H = 7.48 per cent.



*Oxidation of Crotolactone* (m. p.  $75^\circ$ ).—1.4 grams of the crotolactone were dissolved in glacial acetic acid on the water-bath and to the hot solution an excess of chromium trioxide was gradually added. The solution was diluted with water and extracted with ether. The ethereal extract was shaken with a solution of carbonate. On expelling the ether a gummy mass remained, which speedily became crystalline; this was separated by fractional crystallisation from light petroleum into two substances: long, yellow needles of *benzil* (m. p.  $95^\circ$ ) further identified by the mixture melting-point test; and small, colourless crystals of a compound melting at  $165\text{--}166^\circ$ , the quantity of which was insufficient for further investigation.

*Action of Potassium Hydroxide on the Crotolactone* (m. p.  $75^\circ$ ):  
*Formation of*  $\beta$ -Phenyl- $\alpha$ -tert.-butyl- $\beta$ -benzoylpropionic Acid,



(m. p.  $183\text{--}184^\circ$ ).—A quantity of the crotolactone (m. p.  $75^\circ$ ) was heated on the water-bath with alcoholic potassium hydroxide until the alcohol was almost entirely expelled. The product dissolved completely in water, and, on acidifying, an organic acid was precipitated. This substance required repeated crystallisation from alcohol before it could be obtained pure. It crystallises in small prisms or slender needles, melting at  $183\text{--}184^\circ$ . Analysis showed that it had the expected composition.

0.1446 gave 0.4086  $\text{CO}_2$  and 0.0922  $\text{H}_2\text{O}$ . C = 77.07; H = 7.08.

$\text{C}_{20}\text{H}_{22}\text{O}_3$  requires C = 77.42; H = 7.10 per cent.

The alcoholic mother liquor from the foregoing acid deposited a substance melting at  $194\text{--}195^\circ$ , the quantity of which was too small for further investigation.

The *silver salt* of  $\beta$ -phenyl- $\alpha$ -tert.-butyl- $\beta$ -benzoylpropionic acid was obtained as a white precipitate by adding silver nitrate to a solution of the ammonium salt.

0.4354 gave 0.1100 Ag. Ag = 25.26.

$\text{C}_{20}\text{H}_{21}\text{O}_3\text{Ag}$  requires Ag = 25.90 per cent.

*Action of Phenylhydrazine on  $\beta$ -Phenyl- $\alpha$ -tert.-butyl- $\beta$ -benzoylpropionic Acid.*—1.5 grams of the acid and 1 gram of phenylhydrazine were heated in alcoholic solution in a sealed tube for  $2\frac{1}{2}$  hours at  $160^\circ$ . The crystallisation of the product had to be started by rubbing the sides of the tube with a glass rod. The compound crystallised from alcohol in short prisms melting at  $185$ — $186^\circ$ .

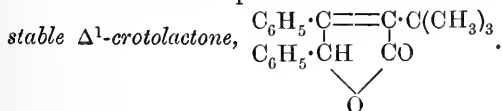
0.1598 gave 0.4756  $\text{CO}_2$  and 0.0983  $\text{H}_2\text{O}$ .  $\text{C} = 81.17$ ;  $\text{H} = 6.83$ .

0.2014 „ 13.00 c.c. moist nitrogen at  $15.5^\circ$  and 756 mm.  $\text{N} = 7.51$ .

$\text{C}_{26}\text{H}_{26}\text{ON}_2$  requires  $\text{C} = 81.67$ ;  $\text{H} = 6.81$ ;  $\text{N} = 7.33$  per cent.

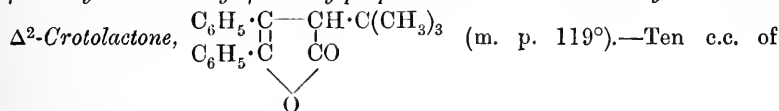
The question of the constitution of this compound is discussed in the introduction to the present paper.

*Dehydration of  $\beta$ -Phenyl- $\alpha$ -tert.-butyl- $\beta$ -benzoylpropionic Acid: Regeneration of the Stable  $\Delta^1$ -Crotolactone* (m. p.  $75^\circ$ ).—A small quantity of the acid (m. p.  $183$ — $184^\circ$ ) was heated in diphenylamine vapour ( $310^\circ$ ) as described in the case of the corresponding experiment with the isomeric ketonic acid, continuing the heating until bubbles of aqueous vapour ceased to be given off. The product, which was slightly coloured, was purified by recrystallisation from alcohol. The quantity was insufficient for complete purification, so that the melting point was found at  $71$ — $72^\circ$ , instead of  $75^\circ$ . A mixture of the substance with a specimen of the pure crotolactone (m. p.  $75^\circ$ ) melted at the intermediate temperature of  $73^\circ$ . The substance was therefore the



By boiling the acid (m. p.  $183$ — $184^\circ$ ) for 4 minutes with fuming hydriodic acid (sp. gr. 1.9) the same dehydration occurred, and the stable  $\Delta^1$ -crotolactone (m. p.  $75^\circ$ ) was obtained. This result was confirmed by the mixture melting-point test. This reaction is precisely the reverse of that which occurs in the case of the crotolactone (m. p.  $150^\circ$ ), as the latter compound is, as already described, hydrolysed by hydriodic acid to the corresponding ketonic acid (m. p.  $133$ — $134^\circ$ ).

*Action of Acetic Anhydride containing a little Sulphuric Acid on  $\beta$ -Phenyl- $\alpha$ -tert.-butyl- $\beta$ -benzoylpropionic Acid: Formation of the Labile*



acetic anhydride were poured over 1.3 grams of the acid (m. p.  $183$ — $184^\circ$ ), and 4 drops of concentrated sulphuric acid were added. After some time, the solution was poured into water. The white solid which was precipitated was recrystallised twice from alcohol; it was thus obtained in long, slender needles, melting at  $119^\circ$ .

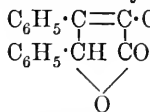
0.1692 gave 0.5112 CO<sub>2</sub> and 0.1053 H<sub>2</sub>O. C = 82.40; H = 6.91.

C<sub>20</sub>H<sub>20</sub>O<sub>2</sub> requires C = 82.19; H = 6.85 per cent.

The yield was 1.1 grams of once recrystallised substance.

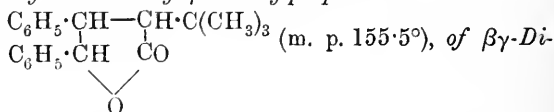
A small quantity of this labile Δ<sup>2</sup>-croto lactone (m. p. 119°) was heated with alcoholic sodium hydroxide on the water-bath. On diluting with water and acidifying, β-phenyl-α-tert.-butyl-β-benzoylpropionic acid was precipitated. It was identified by the mixture melting-point test.

A further quantity of the labile Δ<sup>2</sup>-croto lactone was boiled with acetic anhydride for 2½ hours. The product, precipitated with water and recrystallised from light petroleum, melted at 75–76° and was identified by the mixture melting-point test as the stable Δ<sup>1</sup>-croto lactone, C<sub>6</sub>H<sub>5</sub>·C=C·C(CH<sub>3</sub>)<sub>3</sub>, into which the labile compound had thus been



converted (compare J. Thiele, *Annalen*, 1899, 306, 196).

*Reduction of β-Phenyl-α-tert.-butyl-β-benzoylpropionic Acid: Formation of the Lactone,*



*phenyl-α-tert.-butyl-γ-hydroxybutyric Acid.*—Six grams of the acid (m. p. 183–184°) were dissolved in absolute alcohol, and 8 grams of sodium were gradually added to the boiling solution, which assumed a reddish colour. On adding water a turbidity was produced; this was removed by filtration, and, on acidifying the filtrate, a pasty mass was precipitated which afterwards became hard. The substance was purified by recrystallisation both from alcohol and from light petroleum. From the latter solvent it was deposited in small needles melting at 155.5°. Analysis showed that the hydroxy-acid, formed by reduction of the ketonic acid, had parted with water, yielding the foregoing *butyrolactone*.

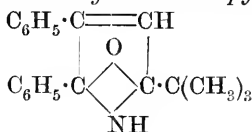
0.1685 gave 0.5022 CO<sub>2</sub> and 0.1143 H<sub>2</sub>O. C = 81.28; H = 7.54.

C<sub>20</sub>H<sub>22</sub>O<sub>2</sub> requires C = 81.63; H = 7.48 per cent.

The first alcoholic mother liquor gave crystals of unaltered acid (m. p. 183–184°) which were removed by extracting with sodium carbonate solution.

VI. *Action of Ammonia and Methylamine on  $\alpha$ -Benzoyl- $\beta$ -trimethacetylstyrene.*

*Action of Ammonia on  $\alpha$ -Benzoyl- $\beta$ -trimethacetylstyrene: Formation of 4:5-Diphenyl-2-tert.-butyl-2:5-oxidopyrrole,*



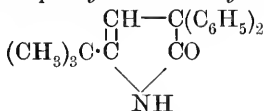
(m.p. 152°).—To a hot saturated, alcoholic solution of 5 grams of benzoyl-trimethacetylstyrene an equal bulk of saturated alcoholic ammonia was added. As the liquid cooled, crystals were deposited. These were filtered off after 24 hours; the filtrate, diluted with water, gave a further crystalline precipitate. By recrystallisation from alcohol the substance was obtained in large, clear, six-sided prisms melting at 152°, and resolidifying even if kept somewhat above that temperature. The yield was about 4 grams.

0.1528 gave 0.4610 CO<sub>2</sub> and 0.1009 H<sub>2</sub>O. C = 82.30; H = 7.33.

0.2594 „ 10.4 c.c. moist nitrogen at 7.5° and 775 mm. N = 4.94.

C<sub>20</sub>H<sub>21</sub>ON requires C = 82.47; H = 7.22; N = 4.81 per cent.

*Action of Heat on 4:5-Diphenyl-2-tert.-butyl-2:5-oxidopyrrole: Formation of 2-Keto-3:3-diphenyl-5-tert.-butyl-2:3-dihydropyrrole,*



(m. p. 220°).—Two grams of the foregoing oxidopyrrole (m. p. 152°) were melted in a paraffin bath and kept at a temperature a little above the melting point. At this temperature the substance speedily resolidified; the product, which was reddish coloured, was boiled with a little alcohol to remove the colouring matter, and the residue was recrystallised from boiling alcohol. It formed long needles, or flat, obliquely truncated prisms melting at 220°.

0.1656 gave 0.4978 CO<sub>2</sub> and 0.1114 H<sub>2</sub>O. C = 81.98; H = 7.47.

0.3044 „ 13.1 c.c. moist nitrogen at 9° and 754 mm. N = 5.10.

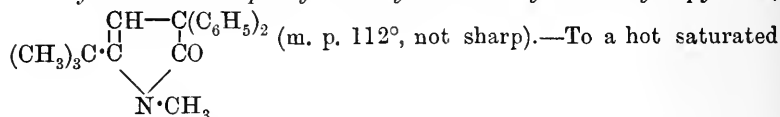
C<sub>20</sub>H<sub>21</sub>ON requires C = 82.47; H = 7.22; N = 4.81 per cent.

The constitution of the foregoing compound is proved by the following synthesis:

Half a gram of the crotolactone,  $\begin{array}{c} \text{CH} - \text{C}(\text{C}_6\text{H}_5)_2 \\ | \quad \quad | \\ (\text{CH}_3)_3\text{C} \cdot \text{C} \quad \text{CO} \\ \quad \quad \diagup \quad \diagdown \\ \quad \quad \text{O} \end{array}$  (m. p.

150°), was heated with strong alcoholic ammonia in a sealed tube at 130° for 3 hours. On cooling, the solution deposited small prisms melting at 219—220°, which proved to be 2-*keto*-3:3-*diphenyl*-5-*tert.*-*butyl*-2:3-*dihydropyrrhole*. The substance was further identified by the mixture melting-point test.

*Action of Methylamine on α-Benzoyl-β-trimethacetylstyrene: Formation of 2-Keto-3:3-diphenyl-1-methyl-5-tert.-butyl-2:3-dihydropyrrhole,*



solution of 4 grams of benzoyltrimethacetylstyrene in absolute alcohol an equal bulk of a 20 per cent. solution of methylamine in alcohol was added. In a few hours crystals separated. Purified by recrystallisation from alcohol they formed stout, eight-sided prisms melting at 112° (not sharp).

0.1546 gave 0.4672 CO<sub>2</sub> and 0.1050 H<sub>2</sub>O. C = 82.41; H = 7.54.

0.2666 „ 10.9 c.c. moist nitrogen at 17° and 744 mm. N = 4.64.

C<sub>21</sub>H<sub>23</sub>ON requires C = 82.62; H = 7.54; N = 4.59 per cent.

A quantity of the substance, heated in a paraffin bath at 150° for 15 minutes, was recovered unchanged.

We have to thank the Council of the Royal Society for an allotment from the Government Grant in aid of the work described in this and the two preceding papers.

CHEMICAL DEPARTMENT,  
UNIVERSITY OF ABERDEEN.

## CLII.—*The Fractional Hydrolysis of Amygdalinic Acid.* *isoAmygdalin.*

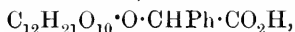
By HENRY DRYSDALE DAKIN.

WHEN two optical antipodes separately combine with a structurally symmetrical substance, they do so with equal velocity, but if they combine with a substance containing an asymmetric group, the speed with which combination occurs may be different in the two cases, and, conversely, the rates of decomposition of the products formed by such reaction may also be unequal.\*

\* The combination of dextro- and lævo-isomerides with a substance containing an asymmetric group does not, however, necessarily take place with unequal speed.

Very few reactions have been described which illustrate these points, the best known being those studied by Marckwald and McKenzie (*Ber.*, 1899, 32, 2130, *Trans.*, 1904, 85, 379), and by Walden (*Ber.*, 1899, 32, 2703). These investigators have shown that the rates of esterification of optically isomeric acids with active alcohols are in many cases different, and also that the rates of hydrolysis of the partially racemic isomeric esters produced by such reactions may be unequal. The present paper gives an account of a reaction which is an example of the complete resolution of a partially racemic glucoside into active compounds without the help of additional optically active substances.

Amygdalinic acid (Liebig and Wöhler, *Annalen*, 1837, 22, 11) is usually assumed to be a maltoside, and the formula



representing it as the maltoside of mandelic acid, is usually accepted.

Amygdalin, the parent substance of amygdalinic acid, gives *l*-mandelic acid on hydrolysis with hydrochloric acid, but amygdalinic acid itself, contrary to expectation, has been shown by J. W. Walker (*Trans.*, 1903, 83, 472) to give inactive mandelic acid. Amygdalinic acid is therefore to be regarded as the maltoside of inactive mandelic acid, or, as is more convenient to assume for the present, a mixture of *d*-mandelic acid maltoside and *l*-mandelic acid maltoside.

It is clear that these two forms, of which amygdalinic acid is assumed to be composed, are not optical antipodes, and, as might be expected, they undergo chemical change at different rates. Although, as previously stated, amygdalinic acid gives inactive mandelic acid on complete hydrolysis, it was found on fractional hydrolysis that the mandelic acid liberated in the early stages was strongly dextrorotatory, whilst the acid liberated towards the close of the reaction was lævorotatory. By suitable methods it was found possible to isolate the pure *d*- and *l*-mandelic acids from the products of hydrolysis, and thus obtain both isomerides from amygdalin by the successive action of barium hydroxide and hydrochloric acid, although amygdalin itself, on direct hydrolysis with acids, yields the lævo-acid almost exclusively.

#### *Preparation and Hydrolysis of Amygdalinic Acid.*

A large number of experiments on the fractional hydrolysis of amygdalinic acid were made which differed slightly in detail, but the following description of an actual experiment may be taken as being fairly typical.

For example, no difference in the rate of change has been observed in the case of reactions which depend simply on the relative affinities of the reacting substances, as in salt-formation between asymmetric acids and alkaloids (Marckwald and Chwolle, *Ber.*, 1898, 31, 783).

Twenty-five grams of amygdalin were heated with a solution of 12.5 grams of crystallised barium hydroxide in 200 c.c. of water until the liberated ammonia was completely expelled. The excess of barium hydroxide was then removed by carbon dioxide and the solution of barium amygdalinate concentrated to 75 c.c. Twenty-five c.c. of hydrochloric acid (sp. gr. 1.16) were now added, the resulting liquid giving a rotation of  $-12.96^\circ$  in a 1 dm. tube. Partial hydrolysis was effected by heating the solution on the water-bath until the rotation in a 1 dm. tube had changed to  $+2.67^\circ$ , this change being completed in about 20 minutes. Under these conditions, rather less than two-thirds of the amygdalinic acid was decomposed. After hydrolysis, the solution was rapidly cooled, and the liberated mandelic acid removed by means of ether in a continuous extraction apparatus; the acid thus obtained, which weighed 4.5 grams and had a specific rotation of  $+17^\circ$  ( $c=5.942$ ;  $\alpha=+1.02^\circ$ ;  $l=1$ ), corresponding with 11 per cent. of the dextro-acid, crystallised readily and was quite free from reducing sugar.

The aqueous solution containing the remainder of the unchanged amygdalinic acid was now heated on the water-bath for an hour in order to complete the hydrolysis; the mandelic acid (about 3 grams) was isolated by ether extraction as before, and gave in aqueous solution containing 5.168 grams in 100 c.c. a rotation of  $-1.07^\circ$  in a 1 dm. tube, whence  $[\alpha]_D = -20.7^\circ$ , corresponding with about 13 per cent. of the laevo-acid.

It is thus clear that the mandelic acid first set free by the hydrolysis of amygdalinic acid is strongly dextrorotatory, and that the acid set free towards the close of the reaction is correspondingly laevorotatory. Numerous experiments were made, which completely confirmed Walker's statement (*loc. cit.*) that the mandelic acid set free on complete hydrolysis is optically inactive.

The more or less active mandelic acids obtained by a repetition of the foregoing experiment were combined, and the approximately pure active acids were isolated by fractionally crystallising both magnesium salts and the acids themselves.

*Isolation of d-Mandelic Acid.*—The mandelic acid formed during the earlier stages of the hydrolysis of amygdalinic acid was converted into the magnesium salt by warming its dilute aqueous solution with magnesium carbonate until the liquid was no longer acid to litmus. On filtering and concentrating, three main crops of crystals were obtained, of which the first, consisting almost entirely of inactive magnesium mandelate, was much the largest. The percentage of magnesium was checked in each crop as a precaution against possible admixture with other acids.

Percentage of Mg in salt dried at 100°, $C_{16}H_{14}O_6Mg$ requires $Mg=7.45$ .	1st Crop. 7.5	2nd Crop. 7.7	3rd Crop. 7.7
Specific rotation in 3 per cent. HCl ...	nil	+29.3	+64.7

The second crop was recrystallised and the mother liquor worked up with the third fraction. The most soluble magnesium salt was finally decomposed with sulphuric acid and the mandelic acid recovered by means of ether. The ethereal extract was evaporated, the residue dissolved in water, filtered from a trace of oily impurity, and slowly concentrated on the water-bath. The mandelic acid was then crystallised repeatedly from water, when the active acid, being less soluble than the racemic acid, separated first. A small quantity of acid was finally obtained, which melted at  $132^\circ$  and had  $[\alpha]_D^{167} +158^\circ$ . There can be no doubt that the substance was practically pure *d*-mandelic acid, which melts at  $132.8^\circ$  and has  $[\alpha]_D^{20} +156.6^\circ$  (Lewkowitsch, *Ber.*, 1883, 16, 1568).

*Isolation of l-Mandelic Acid.*—The mandelic acid set free during the later stages of the hydrolysis of amygdalinic acid was converted into the magnesium salt and fractionated in the manner indicated for the dextro-acid. Three main fractions were obtained, as before, which gave respectively  $Mg=7.3$ ,  $7.6$ , and  $7.6$ , and  $\alpha_D$  in 3 per cent. hydrochloric acid  $-3.0^\circ$ ,  $-7.9^\circ$ , and  $-69.6^\circ$ .

On recrystallising and then recovering the mandelic acid from the most soluble fraction, a product was obtained which melted indefinitely between  $115^\circ$  and  $125^\circ$ . After three recrystallisations from water, the crystals melted at  $131-132^\circ$ , and when examined in aqueous solution had a rotation of  $-152^\circ$ . These constants agree well with those given by Walden, namely, m. p.  $131-132^\circ$ ,  $[\alpha]_D -153^\circ$  (*Zeit. physikal. Chem.*, 1895, 17, 706). These numbers are a little lower than those given by Lewkowitsch (*loc. cit.*).

Although the fractional hydrolysis of amygdalinic acid furnishes a fairly easy method for the preparation of the active mandelic acids, the yield of pure substance is extremely small.

### isoAmygdalin.

Amygdalin, when boiled with concentrated acids, yields *l*-mandelic acid together with glucose and ammonia, but when treated with alkalis in hot solution gives amygdalinic acid (Liebig and Wöhler, *Annalen*, 1837, 22, 11). The latter acid, however, on acid hydrolysis furnishes racemic mandelic acid, and not the *lævo*-modification. J. W. Walker, who first recorded this fact (*Trans.*, 1903, 83, 472), also showed that the racemisation of the mandelic acid part of the glucoside molecule was not a result of the conversion of the nitrile

group into the carboxyl group, for racemisation was complete before this further reaction had taken place. Amygdalin, when dissolved in cold barium hydroxide solution without any evolution of ammonia taking place, was found to yield inactive mandelic acid on subsequent hydrolysis with mineral acids. This apparently catalytic racemisation by means of alkalis recalls the conversion of active hyoscyamine into atropine by means of bases, and of tartaric acid into racemic acid by means of the oxides of iron and aluminium (Will and Bredig, *Ber.*, 1888, 21, 2777; Jungfleisch, *Compt. rend.*, 1877, 85, 805). It is interesting to note that, in being racemised with exceptional ease, amygdalin as a cyanogen derivative, shows a close resemblance to the comparatively few known active halogen compounds (compare Walden, *Ber.*, 1898, 31, 1416). Walker suggested that the first product of the action of alkalis on amygdalin was an isomeric "racemoid" amygdalin, but his attempts to isolate the substance resulted in the production of uncrystallisable gums. This substance has now been isolated in the course of an investigation on the action of enzymes on derivatives of amygdalin. The composition and reactions of the new compound, to which the name *isoamygdalin* is assigned, closely resemble those of the parent substance, as might be expected if the two compounds are optical isomerides.

*isoAmygdalin* is easily prepared by shaking up 5 grams of amygdalin with 25 c.c. of a cold barium hydroxide solution containing 1.25 grams of the crystalline hydroxide. After about 15 minutes, carbon dioxide is passed into the liquid until it is no longer alkaline to phenolphthalein, and the mixture is gently warmed on the water-bath for a few minutes; the precipitated barium carbonate is then removed and the filtrate concentrated to a clear colourless syrup, which, when vigorously stirred with ethyl acetate, slowly yields an almost solid mass of glistening white plates and needles. These crystals are drained on porous earthenware, triturated with more ethyl acetate, and again drained; they retain the ethyl acetate very tenaciously.

For analysis, the substance was dried in a vacuum over phosphoric oxide at about 50°.

0.1605 gave 0.2859 CO<sub>2</sub> and 0.0913 H<sub>2</sub>O. C = 48.7; H = 6.3.

0.1497 „ 0.0413 gram Nitrogen N = 2.7.

C<sub>20</sub>H<sub>27</sub>O<sub>11</sub>N, 2H<sub>2</sub>O requires C = 48.8; H = 6.3; N = 2.8 per cent.

*isoAmygdalin* crystallises with 2 molecules of water, whereas ordinary amygdalin contains 3 molecules of water; this may be removed by heating the substance at a temperature slightly above 100°, but the product is somewhat discoloured, so that it is better to analyse the substance dried to constant weight at a lower tempera-

ture. The substance containing 2 molecules of water of crystallisation has no definite melting point, but at about  $100^{\circ}$  effervescence occurs, water is expelled, and a viscid, glassy mass is left. If, however, the substance is previously dried at  $120^{\circ}$ , it melts gradually on further heating between  $125^{\circ}$  and  $140^{\circ}$  to a slightly yellow, viscid liquid.

*isoAmygdalin*, as was to be expected from Walker's experiments, is lævorotatory. A solution containing 2.688 grams of the crystallised salt in 100 c.c. had a rotation  $-1.28^{\circ}$  in a 1 dm. tube, whence  $[\alpha]_D^{16} -47.6^{\circ}$ . The substance differs very considerably from amygdalin in being extremely soluble in water, readily soluble in ordinary alcohol, much less so in absolute alcohol, and almost insoluble in ethyl acetate. The substance is not easily recrystallised except by almost complete evaporation of the solvent. An aqueous solution does not reduce alkaline copper sulphate solution provided that prolonged boiling and a large excess of alkali are avoided. On adding strong sulphuric acid, the substance, like amygdalin, develops a crimson-red coloration, which disappears on dilution with water. This reaction is considered by Schiff (*Ber.*, 1899, 32, 2699) to be characteristic of the group,  $C_6H_5 \cdot CH(CN) \cdot O-$ .

*isoAmygdalin*, which has a bitter quinine-like taste, indistinguishable from that of ordinary amygdalin, yields ammonia and amygdalinic acid on warming with alkalis, whilst with acids it gives mandelic acid, *d*-glucose, and ammonia. Further details of the hydrolysis by means of acids will be given later.

A proof of the close relationship existing between *isoamygdalin* and amygdalin is the fact that they are both similarly attacked by the enzymes emulsin and maltase. A solution of emulsin was prepared according to Bourquelot's method (*Bull. Soc. Mycol. de France*, 1896, 11, [iii], 199) by macerating mature growths of *Aspergillus niger* with water. After some days, a good deal of autolysis was found to have taken place, and emulsin and other enzymes had dissolved. On adding a little of the liquid to solutions of either amygdalin or *isoamygdalin* and digesting for a short time, the odours of benzaldehyde and hydrocyanic acid were quite marked, and the solution reduced Fehling's solution to a much greater extent than did those from control experiments in which the enzyme had been previously destroyed by boiling. Qualitatively, the two isomerides behaved similarly in yielding the same final products, although it is improbable that the speed of the reaction is the same in both cases.

A solution of maltase was prepared by digesting for one day at  $35^{\circ}$  the emulsion obtained by grinding air-dried yeast with sand and water. Experiments were made in which portions of 5 c.c. of the filtered extract were digested with 0.5 gram of amygdalin or *isoamygdalin*,

control experiments being carried out simultaneously. It was found that after digestion both solutions had a much increased reducing action on Fehling's solution, and crystals indistinguishable from phenylglucosazone were prepared by suitable methods. It is, therefore, probable that the action of maltose on *iso*amygdalin is similar to that on amygdalin (E. Fischer, *Ber.*, 1895, 28, 1509). No attempt was made to isolate the partially racemic mandelonitrile glucoside which, together with *d*-glucose, is probably formed by the action of the enzyme.

The action of acids on *iso*amygdalin is in some respects peculiar. The mandelic acid liberated on complete hydrolysis of the substance with hydrochloric acid was not completely inactive, as one would expect, but distinctly dextrorotatory. This result is the more surprising since amygdalin itself gives *l*-mandelic acid almost exclusively. As an example, the following typical experiment may be described: one gram of *iso*amygdalin and 5 c.c. of hydrochloric acid (sp. gr. 1.12) were heated together for 30 minutes at 80°; the resulting solution was diluted, extracted with ether, and the mandelic acid recovered by evaporation of the solvent; the acid had  $[\alpha]_D +16^\circ$  in aqueous solution. In other experiments differing only in detail, acids were obtained with rotations varying from +8° to +20°.

That the rotations were really due to *d*-mandelic acid and not to traces of glucose was proved by showing that the optical activity persisted after crystallisation of the mandelic acid from a mixture of petroleum and ether.

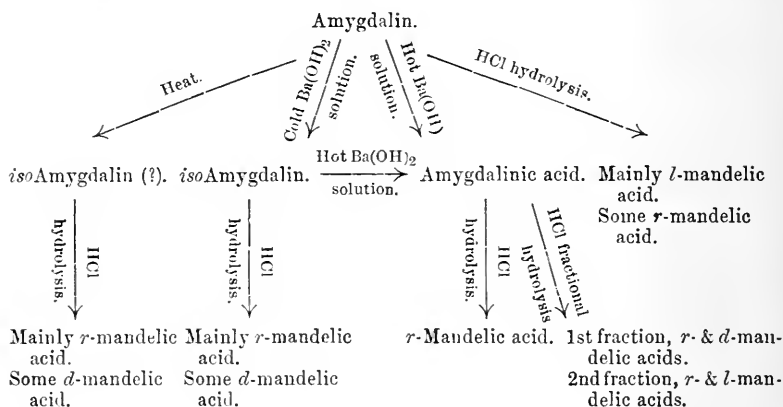
If cold alkalis act on amygdalin to produce a mixture of *i*-mandelonitrile maltoside and *d*-mandelonitrile maltoside, then the production of some *d*-mandelic acid in the hydrolysis of *iso*amygdalin would be readily explained, but such a reaction appears very improbable, although perhaps not impossible in the light of Walden's work on the interaction of bases and active halogen acids. A more probable explanation is that *iso*amygdalin should be considered to be entirely composed of *i*-mandelonitrile *d*-maltoside. This substance may exist as a mixture of the two forms, *d*-mandelonitrile maltoside and *l*-mandelonitrile maltoside. These two forms would not be optical antipodes, and hence would probably be hydrolysed at unequal rates. If now the dextro-compound be assumed to be hydrolysed more rapidly than the lævo-isomeride, at any point short of complete hydrolysis the mandelic acid set free would be dextrorotatory, whilst the unchanged glucoside would contain an excess of its lævo-component. Now it is clear, from what has been previously stated, that this lævo-component, which is ordinary amygdalin, is racemised with extraordinary ease as regards the mandelic acid portion of the molecule, and if it is assumed that this

excess of *l*-mandelonitrile maltoside is being both racemised and hydrolysed, the final result must obviously be the production of a certain amount of *d*-mandelic acid.

This explanation is supported by the fact that when ordinary amygdalin is hydrolysed by acids and the liberated mandelic acid quantitatively recovered, the product, although consisting mainly of *l*-mandelic acid, also contains some of the racemic acid, so that it would appear probable that the hydrochloric acid has the effect of racemising as well as of hydrolysing amygdalin. Moreover, it was found that on fractionally hydrolysing isoamygdalin the first fraction of mandelic acid was dextrorotatory, agreeing with the view that the dextro-glucoside is hydrolysed more readily than the lævo-isomeride, but on completing the hydrolysis the last fraction of mandelic acid was still dextrorotatory, although to a less extent than in the first portion. If racemisation did not occur, one would naturally have expected the last fraction to be lævorotatory, as was the case in the fractional hydrolysis of amygdalinic acid.

There is a great difference between the melting points of amygdalin and isoamygdalin—the former substance melting at  $216^{\circ}$ , the latter indefinitely between  $125^{\circ}$  and  $140^{\circ}$ . Wöhler (*Annalen*, 1842, 41, 155) showed that ordinary amygdalin, solidified after melting, melts again between  $125^{\circ}$  and  $130^{\circ}$ , that is, at about the same temperature as isoamygdalin. It therefore seemed probable that the transformation of amygdalin into the iso-compound could be effected by heat as well as by the action of alkalis. This view was confirmed by showing that, on hydrolysis, Wöhler's "amorphous amygdalin" gave mainly inactive mandelic acid. The compound was prepared by heating amygdalin at  $230^{\circ}$  in a narrow test-tube contained in an oil-bath. The substance melts to a viscid, brown liquid, which sets on cooling to a hard, resinous mass. It was found, on examining the mandelic acid obtained from the hydrolysis of different preparations, that if the amygdalin were only just fused and then immediately cooled, the mandelic acid was still lævorotatory to some extent, but, if on the other hand, the amygdalin were kept fused for several minutes, racemisation of the mandelic acid portion of the molecule was complete, and, as in the case of isoamygdalin, the mandelic acid resulting from hydrolysis was slightly dextrorotatory.

Some of the foregoing transformations of amygdalin are shown in the following diagram :



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## CLII.—*Studies on the Dynamic Isomerism of $\alpha$ - and $\beta$ -Crotonic Acids. Part I.*

By ROBERT SELBY MORRELL and EDWARD KENNETH HANSON.

IN a paper by B. Roozeboom, entitled "Ueber die Erstarrung flüssiger Gemische tautomerer Stoffe" (*Zeit. physikal. Chem.*, 1899, **28**, 288), the theoretical conclusions deduced from the observations of the freezing points of a pair of tautomeric substances are set forth.

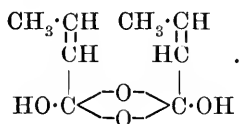
The systems which have been investigated do not, however, illustrate completely the simplest general case described by Roozeboom, as observations have not, to our knowledge, been made on substances in the liquid phase at temperatures much above the melting point of the less fusible component of the system.

Carveth (*J. Physical Chem.*, 1898, **2**, 159, and 1899, **3**, 437), Cameron (*ibid.*, 1898, **2**, 409), Soch (*ibid.*, 1898, **2**, 364), Hollmann (*Zeit. physikal. Chem.*, 1903, **43**, 129), Emerson Reynolds and Werner (*Trans.*, 1903, **83**, 1), and Findlay (this vol., p. 403) have studied cases where decomposition might have ensued at higher temperatures; Hollmann gives the temperature-concentration diagram of acetaldehyde and paracetaldehyde between  $+12.5^{\circ}$  and  $-119^{\circ}$ , but, owing to the boiling point of acetaldehyde being close to the melting point of paracetaldehyde, it was impossible to investigate the equilibrium in the liquid phase above  $12.5^{\circ}$ .

As it is possible to obtain moderate quantities of  $\beta$ -crotonic acid from its quinine salt (Morrell and Bellars, *Trans.*, 1904, 85, 345), we thought that the study of the freezing points of mixtures of the two isomerides would give the composition of the equilibrium mixtures in the liquid state even above the melting point of the  $\alpha$ -crotonic acid, and would furnish a simple and complete confirmation of Roozeboom's theoretical conclusions (Roozeboom, *loc. cit.*, p. 292).

If the velocity of transformation of one isomeride into the other is small for temperatures below  $72^\circ$  (m. p. of  $\alpha$ -crotonic acid), the freezing point curve will resemble those obtained for the benzaldoximes ammonium thiocyanate and thiocarbamide, and acetaldehyde and paracetaldehyde. This velocity at temperatures below  $72^\circ$  is indeed very small, and the addition of  $\alpha$ -crotonic acid to  $\beta$ -crotonic acid, and *vice versa*, depresses the melting point finally to a eutectic point of  $-3^\circ$ .

As the ordinary "isocrotonic" acid does not solidify at  $-20^\circ$ , it seemed probable that at temperatures above  $72^\circ$  a compound of the two acids might be formed, and the substance having so low a freezing point might be this compound mixed with quantities of one or other of the two isomerides. Wislicenus (*Chem. Centr.*, 1897, ii, 259) suggested that the compound not solidifying at  $-20^\circ$  might have the formula:



The preliminary experiments on the equilibrium in the liquid phase seem to indicate that no such compound is formed below  $170^\circ$ , although before this can be decided it will be necessary to investigate the mixtures obtained between  $138^\circ$  and  $145^\circ$  (see p. 1525). In case the evidence against the formation of the compound in the liquid mixture is strengthened, there still remains the possibility that it might condense from a mixture of the two isomerides in the state of vapour such as would be obtained on distillation.

If a compound were formed below  $72^\circ$ , the form of the temperature-concentration diagram would show two minima (compare Philip, *Trans.*, 1903, 83, 829, the diagram for phenol and *p*-toluidine), or might show a point of inflexion in the case of the melting point of the compound being higher than its transition point to one of the other solid phases (see Findlay, *Phase Rule*, p. 208, and Fig. 64, p. 207). No such second minimum or point of inflexion has been observed, and the conclusion which must be drawn is that no compound of  $\alpha$ - and  $\beta$ -crotonic acids is formed below  $72^\circ$ .

When working between  $100^\circ$  and  $168^\circ$  in our preliminary experi-

ments, we found that the  $\beta$ -crotonic acid changed at first slowly and then rapidly, until at the latter temperature only 28 per cent. of the  $\beta$ -acid remained; moreover, the  $\alpha$ -crotonic acid, heated to  $168^\circ$ , was found to contain 24 per cent. of the  $\beta$ -acid. The composition of the mixture at any intermediate temperature is easily found by cooling it rapidly, determining its freezing point, and observing the form of the crystals. The two crotonic acids boil over together between  $168^\circ$  and  $174^\circ$  (Michael, *loc. cit.*), and our equilibrium curves meet at  $172^\circ$ .

Michael (*loc. cit.*) found that on heating  $\beta$ -crotonic acid the amount of  $\alpha$ -crotonic acid produced could be estimated by means of its sodium salt, this being insoluble in absolute alcohol. His numbers agree moderately with those obtained by us, but Michael continued the heating for 36 hours, whilst in our experiments the acid was merely heated for 6 hours; hence his numbers should be higher than ours.

Temperature.	Percentage of $\alpha$ -crotonic acid.	
	Michael	Morrell and Hanson.
100°	0	2.5
136°	34	20
162°	66	63
182°	67.5	—

In reference to the acid which does not solidify at  $-20^\circ$ , it may be said that, although the freezing point of the mixture after heating to  $145^\circ$  was  $-3.1^\circ$ , still the whole did not become solid even after cooling to  $-19^\circ$ . At  $145^\circ$ , the composition of the mixture is 70 per cent.  $\beta$ -crotonic and 30 per cent.  $\alpha$ -crotonic acid, when starting with  $\beta$ -crotonic acid. It will be necessary to investigate the composition of the mixture between  $138^\circ$  and  $145^\circ$  more carefully in order to decide whether there is a compound formed between these temperatures.

It is proposed to investigate further the velocity of change at any temperature, and also to determine the "natural freezing point" of the system of mixed  $\alpha$ - and  $\beta$ -crotonic acids.

#### EXPERIMENTAL.

$\beta$ -Crotonic acid was prepared from barium  $\beta$ -crotonate (Morrell and Bellars, *loc. cit.*), and the ethereal solution dried thoroughly over fused calcium chloride. After evaporating the ether under reduced pressure, a colourless, mobile liquid, with a peculiar pungent smell, was obtained. The sample used froze at  $14.96^\circ$  (corr.), and, since Wislicenus' acid melted at  $15.1^\circ$ , there seemed little doubt that we were dealing with the anhydrous acid, which is most probably identical with

Michael's acid because it gave no precipitate in alcoholic solution with concentrated alcoholic soda,

*Determination of the Freezing Point Curves.*

The freezing point was determined in an ordinary Beckmann's apparatus, and an alcohol thermometer, graduated in tenths between  $20^{\circ}$  and  $-50^{\circ}$ , was used. All the thermometers employed were standardised at the National Physical Laboratory. A mixture of 270 grams of sodium nitrate, 200 grams of ammonium thiocyanate, and 500 grams of ice gave a temperature of  $-21^{\circ}$ , which rose to  $-5^{\circ}$  after 6 hours, and consequently was a most convenient cooling agent.

A known weight of the sample of  $\beta$ -crotonic acid, melting at  $14.96^{\circ}$ , was treated with weighed amounts of the pure acid. The  $\alpha$ -crotonic acid, supplied by Königs, was carefully dried on a tile for a week, and melted sharply at  $72^{\circ}$  (corr.).

The figures obtained in one series of experiments are :

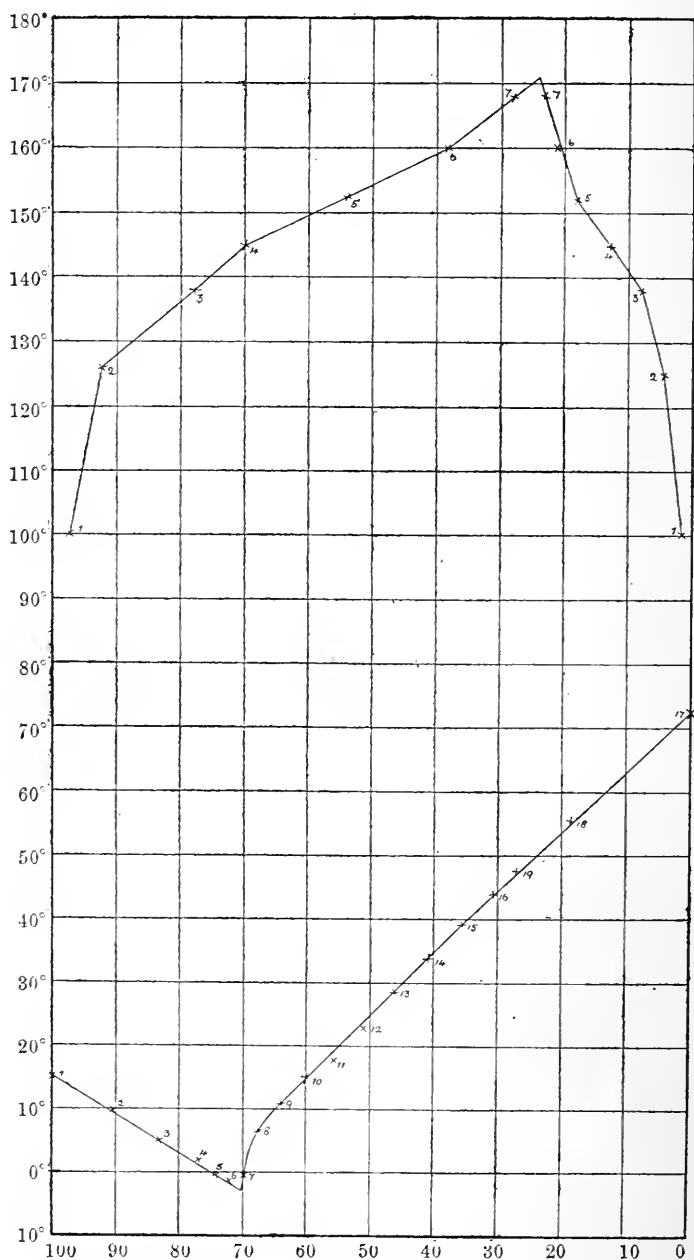
Weight of $\alpha$ -acid added.	Total weight of $\alpha$ -acid added.	Total weight of 2 acids.	Percentage of $\beta$ -acid.	Freezing point of mixture (corr.).
0	0	5.0877	100	+14.96°
0.5322	0.5322	5.6199	90.5	+ 9.6
0.4963	1.0285	6.1162	83.2	+ 5.28
0.4624	1.4909	6.5786	77.35	+ 1.95
0.2325	1.7234	6.8111	74.7	- 0.25
0.2492	1.9726	7.0603	72.05	- 1.25
0.2523	2.2249	7.3126	69.6	- 0.65
0.2419	2.4668	7.5545	67.3	+ 6.48
0.4008	2.8676	7.9553	63.95	+10.5
0.5283	3.3959	8.4836	59.97	+14.7

At this point it was necessary to substitute a mercury thermometer, graduated in tenths, for the alcohol thermometer, and the tube containing the mixture of 59.97 per cent. of  $\beta$ -crotonic acid was again weighed and the experiment continued :

Weight of $\alpha$ -acid added.	Total weight of $\alpha$ -acid added.	Total weight of 2 acids.	Percentage of $\beta$ -acid.	Freezing point of mixture (corr.).
0.5369	3.9097	8.9598	56.47	+17.25°
0.7936	4.7033	9.7534	51.8	+22.64
0.9750	5.6783	10.7284	47.0	+28.64
1.4539	7.1322	12.1823	41.4	+33.64
1.8128	8.9450	13.9953	36.1	+38.87
2.3840	11.3290	16.3791	30.8	+43.96

In order to complete the diagram, a weighed amount of  $\alpha$ -crotonic acid was taken, and weighed quantities of  $\beta$ -crotonic acid added :

Weight of $\beta$ -acid added.	Total weight of $\beta$ -acid added.	Total weight of 2 acids.	Percentage of $\beta$ -acid.	Freezing point of mixture (corr.).
0	0	3.7944	0	+71.96°
0.8468	0.8468	4.6412	18.2	+55.71
0.5495	1.3963	5.1917	26.9	+47.52



Temperature concentration diagram of  $\alpha$ - and  $\beta$ -crotonic acids.

In determining these curves, the following points were noticed :

Between  $+15^{\circ}$  and  $-1.1^{\circ}$ , the solid separating out consisted of long, needle-shaped crystals, which are characteristic of  $\beta$ -crotonic acid. Between  $-1.1^{\circ}$  and  $-0.05^{\circ}$ , the mixture froze to a peculiar curdy solid, whilst beyond  $-0.05^{\circ}$  granular aggregates of broad, prismatic crystals of  $\alpha$ -crotonic acid separated out. At  $15^{\circ}$ , the pure  $\beta$ -crotonic acid showed markedly the phenomenon of supercooling.

The latent heat of fusion of the mixture of  $\alpha$ - and  $\beta$  crotonic acids appeared to be small, since the rise in temperature on solidification was very slight.

The freezing point of each mixture given in the table remained the same during several duplicated determinations, showing that the velocity of transformation was negligibly small at the temperatures observed.

If the  $\beta$ -crotonic acid is not perfectly dry, the eutectic point is much lower. In two experiments with acid which had not been dried by calcium chloride, the original freezing points were  $0.5^{\circ}$  and  $13^{\circ}$ , and the corresponding eutectic points were  $-8^{\circ}$  and  $-4^{\circ}$ , but the form of the curves obtained by adding  $\alpha$ -crotonic acid was parallel to those furnished by the dry acid.

*The Action of Heat on  $\alpha$ - and  $\beta$ -Crotonic Acids between  $100^{\circ}$  and  $168^{\circ}$ .*

Two tubes, one containing  $\alpha$ -crotonic acid and the other the  $\beta$ -acid, were sealed and heated at  $100^{\circ}$  for six hours in an oil-bath. The contents were cooled rapidly and their freezing points determined. The  $\beta$ -crotonic acid solidified at  $+13.6^{\circ}$  and the  $\alpha$ -crotonic acid at  $+70.5^{\circ}$ .

The two tubes were again sealed and heated at  $126^{\circ}$  in an oil-bath. The freezing point of the  $\beta$ -crotonic acid had fallen to  $+10.8^{\circ}$  and that of the  $\alpha$ -acid to  $+68.4^{\circ}$ . After six hours' heating at  $138^{\circ}$  and rapidly cooling, the  $\beta$ -acid froze at  $+3.1^{\circ}$  and the  $\alpha$ -acid at  $+64.8^{\circ}$ . At  $145^{\circ}$ , the  $\beta$ -crotonic acid froze at  $-3.1^{\circ}$ , and the  $\alpha$ -isomeride at  $+60.3^{\circ}$ . The solid separating out during the determination of the freezing point of the  $\beta$ -crotonic acid in this case resembled that obtained in the earlier part of the research at the temperature of the eutectic point.

After six hours at  $152^{\circ}$ , the melting point of the  $\beta$ -crotonic acid rose to  $+21^{\circ}$ , while that of the  $\alpha$ -acid was depressed to  $+55.8^{\circ}$ . The acid had darkened in colour, but there was no difficulty in obtaining a sharp freezing point.

At  $160^{\circ}$ , the melting point of the  $\beta$ -acid showed a further rise to  $+37.6^{\circ}$ , and the  $\alpha$ -acid a fall to  $+52.8^{\circ}$ . At  $168^{\circ}$ , the melting points

of the two acids were only  $5^{\circ}$  apart, the  $\beta$ -crotonic acid freezing at  $+46^{\circ}$  and the  $\alpha$ -acid at  $+51^{\circ}$ .

At  $172^{\circ}$ , the two would possess the same boiling point, and would consist of a mixture of 76 per cent.  $\alpha$ -crotonic acid and 24 per cent. of the  $\beta$ -acid. The boiling point of the equilibrium mixture of  $\alpha$ - and  $\beta$ -crotonic acids is given by Michael (*J. pr. Chem.*, 2, 46, 236) as  $168-174^{\circ}$ , and must, from our experiments, consist of 76 per cent. of  $\alpha$ -acid and 24 per cent. of the  $\beta$ -acid.

As in the experiments conducted below  $72^{\circ}$ , it is quite easy to decide, from the crystalline form of the solid which separates out at the melting point, which of the two isomerides constitutes the solvent.

Our thanks are due to the Research Fund Committee of the Chemical Society for a grant defraying the expenses of this work.

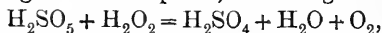
GONVILLE AND CAIUS COLLEGE LABORATORY,  
CAMBRIDGE.

### CLIII.—*The Effect of Colloidal Platinum on Mixtures of Caro's Persulphuric Acid and Hydrogen Peroxide.*

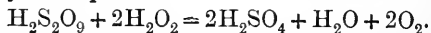
By THOMAS SLATER PRICE and JOHN ALBERT NEWTON FRIEND.

MANY investigations have been carried out with the object of determining the composition of Caro's acid, and the results show that its formula is probably either  $\text{H}_2\text{SO}_5$  or  $\text{H}_2\text{S}_2\text{O}_9$  (see Price, *Trans.*, 1903, 83, 543; Mugdan, *Zeit. Elektrochem.*, 1903, 9, 980).

When colloidal platinum is added to mixtures of Caro's acid and hydrogen peroxide, oxygen is rapidly evolved. The authors thought that, by studying this reaction, it might be possible to decide between the two formulæ suggested. If the formula were  $\text{H}_2\text{SO}_5$ , a reaction of the second order might be anticipated, according to the equation



but if it were  $\text{H}_2\text{S}_2\text{O}_9$ , one would expect a reaction of the third order, as represented by the equation



As will be seen from the results obtained, the formula cannot be determined in this way, as it has not been found possible to obtain constants of any order.

*Preparation of Caro's Acid.*—Pure, dry, and finely-powdered potassium persulphate was placed in an evaporating basin, imbedded

in a mixture of ice and salt, 5 c.c. of concentrated sulphuric acid were then added, drop by drop, from a pipette; this operation required about 10 minutes and the mixture was well stirred the whole time. After about an hour, the mixture was slowly poured on to broken ice, contained in a large evaporating basin, also imbedded in ice and salt, and the diluted mixture was left for three or more hours and made up to 250 c.c. with distilled water. When left for a few hours longer, the solution was ready for use. It was then free from hydrogen peroxide, for it gave no coloration with a solution of titanium sulphate. This method of preparation was essential, since hydrogen peroxide, in the presence of Caro's acid, cannot be estimated by titration with potassium permanganate (Price, *Trans.*, 1903, 83, 543; Friend, *Trans.*, 1904, 85, 597) and it is obviously necessary to know the strength of the two components in the mixtures used.

The colloidal platinum was prepared in the usual way (Bredig, *Zeit. physikal. Chem.*, 1899, 31, 258). The hydrogen peroxide (30 per cent. solution) was obtained from Merck and guaranteed to be pure.

As the progress of the reaction cannot be measured by titration of the hydrogen peroxide with permanganate, an attempt was made to estimate the hydrogen peroxide colorimetrically by means of titanium sulphate. It was found, however, that the results could not be depended on to within 8 per cent.

The velocity of reaction was finally determined by measuring the rate at which the oxygen was evolved from the mixture, all the determinations being carried out at 25°. The apparatus used is represented in the figure. The mixture was contained in the tube, *A*. The evolved oxygen escaped through *B* to the burette, *C*, which was surrounded by a water-jacket, through which a slow stream from the thermostat was caused to circulate. The level of the water in *C* was adjusted by means of the india-rubber tube, *D*, and reservoir, *E*; the tube, *A*, was closed by an india-rubber cork through which passed a stirrer, the whole being made air-tight by means of a mercury seal.

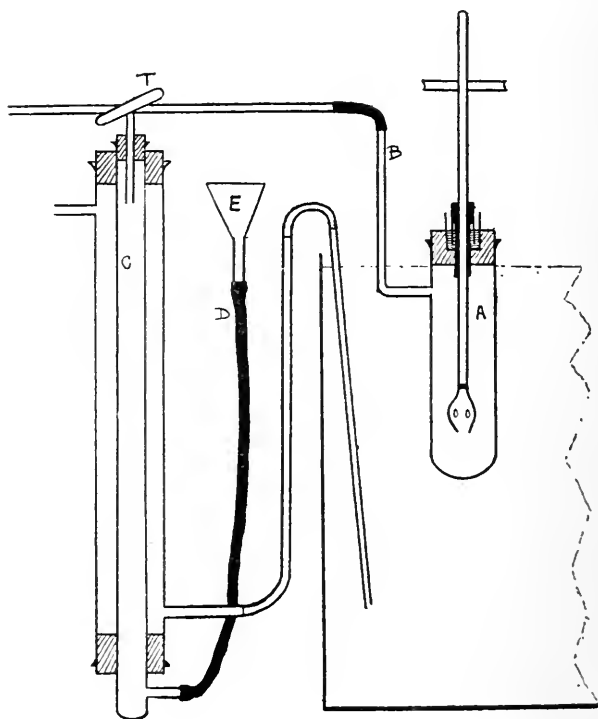
The strength of the Caro's acid was determined by the liberation of iodine from potassium iodide; that of the hydrogen peroxide by titration with permanganate.

The two solutions were then mixed in *A* and left for 10 minutes, before the addition of platinum. It was only after numerous experiments that we found this to be the only means by which we could obtain two comparable series of results. At present we are unable to explain this action, for in the absence of platinum, as will be seen from the following table, no appreciable reaction takes place between the two substances in so short a time.

TABLE I.

Mixtures of Caro's acid and hydrogen peroxide were employed, quantities of 5 c.c. being titrated at intervals with  $N/50 \text{ KMnO}_4$ .

Time of titration.	Mixture I.	Mixture II.	Mixture III.
Directly after mixing	13.06 c.c.	10.80 c.c.	12.70 c.c.
15 mins. „ „	13.28 „	10.82 „	12.78 „
30 mins. „ „	13.30 „	10.79 „	12.90 „
60 mins. „ „	13.31 „	10.81 „	13.00 „
18 hours „ „	13.36 „	—	12.93 „



The small differences are probably due to experimental error (Friend, *loc. cit.*).

In the following series, the stirring was vigorous, and Bredig and Walton have since shown (*Zeit. physikal. Chem.*, 1904, 47, 185) that under these conditions accurate results may be obtained. Table II shows how nearly two comparable experiments agree.

TABLE II.

Time in minutes.	Volume I in c.c.	Volume II in c.c.	Time in minutes.	Volume I in c.c.	Volume II in c.c.
15	3.12	3.06	41	7.23	7.10
19	3.87	3.88	45	7.67	7.56
22	4.38	4.40	55	8.70	8.58
28	5.38	5.38	65	9.18	9.07
34	6.30	6.22			

In the following tables :

$t$  = time in minutes after adding the platinum.

$v$  = volume of oxygen evolved at N.T.P.

$A$  = concentration of peroxide, measured as the no. of c.c. of oxygen present in the mixture.

$B$  = concentration of Caro's acid similarly expressed.

$k_2$  = velocity constant of the second order.

$k_3$  = velocity constant of the third order.

$R$  = extent to which the action has proceeded (approximately).

The concentration of the platinum in the mixture was in all cases 1 gram-atom in 227,000 litres.

TABLE III.

(Feb. 25) $A=9.34$ $B=20.29$ .			(Feb. 26) $A=23.37$ $B=20.29$ .		
$t$ .	$v$ .	$k_2$ .	$t$ .	$v$ .	$k_2$ .
16	4.71	—	16	5.54	—
20	5.88	0.000542	20	6.69	0.000180
24	7.00	0.000563	25	7.90	0.000169
29	8.38	0.000583	31	9.14	0.000161
35	9.63	0.000597	37	10.24	0.000154
42	10.97	0.000613	44	11.38	0.000149
50	12.39	0.000650	53	12.55	0.000140
55	13.12	0.000665	63	13.70	0.000133
60	13.89	0.000698	77	15.10	0.000127
70	15.13	0.000760	92	16.43	0.000121
80	16.27	0.000848	100	16.99	0.000118

TABLE IV.

	$A$ .	$B$ .	$k_2$ .	$R$ .
(Feb. 10).....	16.24	12.65	0.000354—0.000362	1/4
(Feb. 10).....	7.26	12.65	0.000595—0.000840	1/3
(Feb. 13).....	5.29	29.23	0.000448—0.000490	1/4
(Feb. 13).....	13.71	29.23	0.000295—0.000377	1/2

Only two series are given in full, it being deemed sufficient to give merely the general nature of the others. It will be observed that there is no approach to constancy in the values for  $k_2$ . The constants rise gradually, except in the case of the series for February 26. Ex-

periments carried out after this date with the same platinum solution likewise showed a decrease in the values for  $k_2$ . It occurred to us that this was probably due to some of the platinum being thrown out of the colloidal solution by the electrolytes present. To test this, we made a solution of platinum containing about 0.5 grams of gelatin per litre (Zsigmondy, *Annalen*, 1898, 301, 387; *Zeit. physikal. Chem.*, 1901, 40, 697; Bredig, *Zeit. angew. Chem.*, 1898, 953; Kuspert, *Ber.*, 1902, 35, 2815 and 4066; Paal and Amberger, *Ber.*, 1904, 37, 124; Bredig and Fortner, *Ber.*, 1904, 37, 798), and kept it in a steriliser at 80–90° to prevent bacterial or fungoid growth.

The results obtained with this solution are given in the following tables:

TABLE V.

$A=28.74. \quad B=19.72.$				$A=15.93. \quad B=20.93$			
$t.$	$v.$	$k_2.$	$k_3.$	$t.$	$v.$	$k_2.$	$k_3.$
16	3.10	—	—	15	2.52	—	—
18	3.65	0.000124	—	18	3.00	0.000123	0.0000195
20	4.20	0.000126	0.0000109	21	3.48	0.000122	0.0000198
26	5.83	0.000132	0.0000116	27	4.42	0.000127	0.0000204
32	7.52	0.000135	0.0000122	34	5.47	0.000128	0.0000212
33	9.16	0.000142	0.0000129	42	6.65	0.000131	0.0000222
44	10.71	0.000146	0.0000135	50	7.90	0.000137	0.0000239
50	12.08	0.000147	0.0000139	60	9.20	0.000139	0.0000250

TABLE VI.

$A.$	$B.$	$k_2.$	$R.$
17.54	19.72	0.000183 — 0.000224	2/5
16.97	14.05	0.0000916 — 0.000136	3/5
16.97	22.15	0.0000865 — 0.0000972	2/5
27.98	14.24	0.0000735 — 0.0000865	3/10
27.98	24.95	0.0000446 — 0.0000508	1/3
13.99	27.58	0.000194 — 0.000242	3/7
21.09	21.09	0.0000143 — 0.0000210	5/14

A glance at the foregoing tables shows that the addition of gelatin has caused all the constants to rise gradually. As neither  $k_2$  nor  $k_3$  shows any approach to constancy, it is impossible to determine to which order the action belongs.

The gradual rise in the constants might be attributed to separate catalytic decomposition of the Caro's acid and peroxide, each taking place independently; but the following results negative this view. Colloidal platinum was allowed to act on separate solutions of Caro's acid and hydrogen peroxide.

TABLE VII.

$A=9\cdot34.$		$B=20\cdot29.$	
$t.$	$v.$	$t.$	$v.$
12	0.18	12	0.28
16	0.26	16	0.36
22	0.34	22	0.39
29	0.45	29	0.44
38	0.61	38	0.47
50	0.69	50	0.50
65	0.88	65	0.52
92	1.09	92	0.54

If these results are compared with those in Table III, it will be seen that the sum of the volumes of oxygen evolved from the independent decomposition of the peroxide and Caro's acid is much less than that evolved from a mixture of the two.

That the hydrogen peroxide and Caro's acid both disappear will be evident from a consideration of the following results: 5 c.c. of a mixture were titrated with  $N/50$  permanganate, some potassium iodide solution was then added, and the Caro's acid present estimated by titration of the liberated iodine with  $N/50$  sodium thiosulphate solution. The titrations were effected under the same conditions, so that they might be comparable with each other (Friend, *loc. cit.*).

The columns headed  $x$  and  $y$  represent the diminution in the titration values.

TABLE VIII.

$t.$	Permanganate.	$x.$	Thiosulphate.	$y.$	$y/x.$
3	14.20 c.c.	—	16.01 c.c.	—	—
23	10.70 "	3.50	12.84 "	3.17	0.91
28	9.53 "	4.67	11.70 "	4.31	0.92
33	8.68 "	5.52	10.98 "	5.03	0.91
39	7.80 "	6.40	10.17 "	5.84	0.91
45	7.08 "	7.12	9.44 "	6.57	0.92
51	6.48 "	7.72	8.91 "	7.10	0.92
58	5.90 "	8.30	8.38 "	7.63	0.92
65	5.30 "	8.90	7.79 "	8.22	0.92

Since the ratio  $y/x$  remains constant, it is clear that the amounts of the two substances decomposed are connected with each other. We have carried out a number of similar experiments with precisely the same results.

The increase in the velocity constants is probably due to two causes:—

(1) Increase in the activity of the platinum during the reaction, a phenomenon noticed by Bredig and his fellow workers (compare Liebermann, *Ber.*, 1904, 37, 1519; Vondráček, *Zeit. anorg. Chem.*, 1904, 37, 1519; Bredig and Fortner, *loc. cit.*).

(2) The independent catalytic decomposition of the peroxide superposed on the reaction between the two reagents.

Using a large excess of one of the components, we have carried out a number of experiments to see if the order of the reaction could be determined in this way, but no definite conclusions can be drawn from the results.

*Concentration of Platinum.*

The following table gives the results obtained by varying the concentration of the platinum, that of the hydrogen peroxide and Caro's acid being kept constant. The series are not given in full, this being deemed unnecessary.

$Pt$  = number of gram-atoms of platinum in 764,000 litres.

$t_1$  and  $t_2$  = times in minutes for evolution of 5 and 10 c.c. of oxygen respectively.

$Pt.$	$t_1.$	$t_2.$	$Pt.$	$t_1.$	$t_2.$
1	204	—	6	55	106
2	141	300	7	49	93
3	77	162	8	40	73
4	66	133	9	31	57
5	57	111	—	—	—

It will be observed that there is no simple connection between the concentration of the platinum and the volume of oxygen evolved. It should be borne in mind, however, that the results are not strictly comparable, the experiments having been carried out on different days, so that the catalytic effect of the platinum had probably undergone a slight change. Moreover, the platinum solution was, of necessity, diluted to a different extent in each case, and this would have an influence on the catalytic effect (Bredig and Müller von Berneck, *Zeit. physikal. Chem.*, 1899, 31, 258).

*Effect of Acidity.*—The alteration in the concentration of sulphuric acid has apparently little effect, as will be seen from the following results :

$t.$	$v_1$ , total acidity 0.5 m.*	$v_2$ , total acidity m.	$v_3$ , total acidity 1.5 m.
10	1.52	1.45	1.40
18	3.50	3.62	3.60
26	5.90	5.70	5.82
34	8.16	7.80	7.95
42	10.10	9.78	9.90
60	13.83	13.72	13.80

\* m=molecular weight of acid in grams per litre of solution.

*Effect of Alkalinity.*—We could not obtain any satisfactory results, since the velocity of decomposition seemed to depend on the rate of stirring.

*Effect of Poisons.*—We have made a few experiments, using hydrocyanic acid and sulphuretted hydrogen as poisons, and obtained results similar to those of Bredig (Bredig and Ikeda, *Zeit. physikal. Chem.*, 1901, 31, 1).

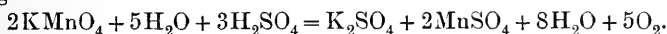
THE UNIVERSITY,  
BIRMINGHAM.

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CLIV.—*Note on the Influence of Potassium Persulphate on the Estimation of Hydrogen Peroxide.*

By JOHN ALBERT NEWTON FRIEND.

IN a recent communication (Trans., 1904, 85, 597), the author showed that in ordinary circumstances a correct estimate of hydrogen peroxide in the presence of potassium persulphate is not obtained by titration with potassium permanganate, for under these conditions the amount of permanganate required always falls short of the theoretical amount (Price, Trans., 1903, 83, 546). The equation usually given as representing the reaction between hydrogen peroxide and potassium permanganate in acid solution is :



As is well known, however, manganese sulphate plays some part in the reaction, and a small quantity of this substance is frequently added to facilitate the titration in dilute solution (Lowry and West, Trans., 1900, 77, 950). But in the presence of potassium persulphate, some other reaction must occur to account for the disappearance of some of the hydrogen peroxide, already noticed.

It seemed of interest to ascertain whether any of the potassium persulphate was decomposed during a titration, although pure solutions of potassium persulphate and potassium permanganate have no appreciable effect on one another when mixed in the cold.

To do this, 20 c.c. of a solution containing known quantities of hydrogen peroxide and potassium persulphate were titrated at varying velocities (Trans., 1904, 85, 598) with *N*/50 potassium permanganate. A known quantity of ferrous sulphate in acid solution was then added and the mixture heated to boiling ; by this means, the potassium persulphate was decomposed, the amount being estimated by titrating the excess of ferrous sulphate with permanganate (Price and Denning, *Zeit. physikal. Chem.*, 1903, 46, 96).

The results are embodied in the table on p. 1534.

Column I gives the no. of c.c. of permanganate required to decompose the hydrogen peroxide.

Column II gives the amount of permanganate which would have been required had no persulphate been present.

Column III gives the difference between I and II, that is, the amount of hydrogen peroxide not accounted for.

Column IV gives the amount of ferrous sulphate solution required to decompose the persulphate.

Column V gives the equivalent of the persulphate originally added in terms of the ferrous sulphate solution.

Column VI gives the difference between IV and V, that is, the amount of persulphate decomposed during the titration.

I.	II.	III.	IV.	V.	VI.
11.90	12.60	0.70	14.46	15.20	0.74
10.73	12.60	1.87	13.47	15.20	1.73
10.61	12.60	1.99	13.17	15.20	2.03
10.20	12.60	2.40	12.76	15.20	2.44
9.70	12.60	2.90	12.27	15.20	2.93
22.60	24.32	1.72	13.46	15.20	1.74
22.45	24.32	1.87	13.28	15.20	1.92
21.68	24.32	2.64	12.49	15.20	2.71
21.59	24.32	2.73	12.47	15.20	2.73
34.92	36.90	1.98	13.19	15.20	2.01
33.70	36.90	3.20	11.97	15.20	3.23
33.63	36.90	3.22	11.95	15.20	3.25
21.52	21.80	0.28	21.98	22.26	0.28
21.10	21.80	0.70	21.57	22.26	0.69
20.26	21.80	1.54	20.66	22.26	1.60
19.37	21.80	2.43	19.94	22.26	2.32
18.81	21.80	2.99	19.35	22.26	2.91
17.97	21.80	3.83	18.50	22.26	3.76
16.32	21.80	5.48	16.95	22.26	5.31
14.82	21.80	6.98	15.43	22.26	6.83
14.00	21.80	7.80	14.47	22.26	7.79
13.09	21.80	8.71	13.68	22.26	8.58

A glance at the foregoing data shows that columns III and VI are almost identical, so that for every molecule of hydrogen peroxide not accounted for by titration with permanganate a molecule of persulphate disappears. This suggests the reaction :



which takes place when pure hydrogen peroxide and potassium persulphate solutions are mixed (Price and Denning, *loc. cit.*). This reaction is, however, very slow, and, during the few seconds occupied by a titration, would be inappreciable. It seems probable, therefore, that it is catalytically accelerated by some oxide of manganese formed

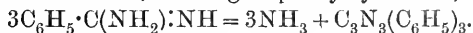
during titration (compare Schilow, *Ber.*, 1903, 36, 2735). In this way we may account for the fact that in ordinary circumstances hydrogen peroxide cannot be estimated by titration with potassium permanganate in the presence of potassium persulphate.

GRAMMAR SCHOOL,  
WATFORD.

## CLV.—*The Action of Nitrogen Sulphide on Organic Substances. Part II.*

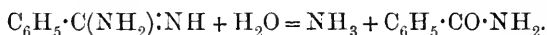
By FRANCIS ERNEST FRANCIS and OLIVER CHARLES MINTY DAVIS.

FURTHER investigation of the action of nitrogen sulphide on anisaldehyde has confirmed our suspicion (this vol., p. 261) that tri-*p*-methoxyphenylecyanidine was a product of this condensation, being produced in somewhat larger proportion than we had previously supposed. Another product, anisamidine sulphate, which was contaminated with small quantities of ammonium sulphate, was separated by taking advantage of its solubility in hot water, and characterised by the preparation of the corresponding chloride, nitrate, and platinichloride. We were not, however, able to isolate pure anisamidine from its salts, for the base we obtained, although readily soluble in water and having the strongly basic properties characteristic of the amidines, had a melting point 6—7° higher than that given by Lossen, and, moreover, it gave unsatisfactory analytical data. But as its aqueous solution gave rise to anisamide and ammonia, the reaction occurring slowly in the cold and immediately on warming, this fact was sufficient proof that the substance under examination was actually anisamidine, although in an impure state. The unexpected and singular formation of an anisamidine salt when nitrogen sulphide acts on the aldehyde led to the supposition that such derivatives might be intermediate products in the formation of the cyanidines, since, on heating, the amidines lose ammonia and are converted into the corresponding polymerised nitriles, which in this case are cyanidines. Thus benzamidine begins to evolve ammonia at 115°, forming triphenylecyanidine,



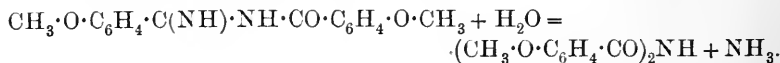
Consequently we again tried the action of nitrogen sulphide on benzaldehyde under varying conditions, but up to the present we have obtained no indication of the formation of a benzamidine salt. It seems, however, quite probable that the small amount of substance obtained in this reaction and described as being soluble in water and melting at 128° was benzamide (see this vol., p. 262). We have since

found that it evolves ammonia on warming with caustic potash, the solution giving rise on acidification to a substance having the properties of benzoic acid. This amide may have been formed by the action of benzamidine on water :

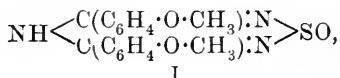


But if this suggestion is correct, the amount of benzamide obtained was so small that only very little benzamidine could have been formed in the reaction. Moreover, the amount of ammonia obtained as ammonium sulphate in the experiments with either benzaldehyde or anisaldehyde is much less than would be expected had the formation of the cyanidine derivatives proceeded on the lines indicated. We are as yet unable to explain the oxidation that obviously takes place in this reaction. Sulphur dioxide is evolved, but, both with benzaldehyde and anisaldehyde, ammonium sulphate is formed to a greater extent in the former than the latter. Moreover, in the case of anisaldehyde, anisamidine sulphate is also produced. It is hoped that further investigation will elucidate this point.

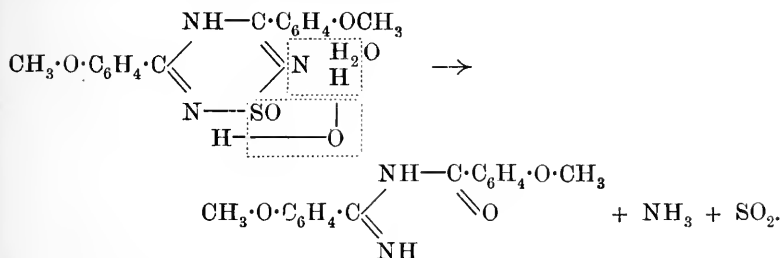
An insoluble, definitely crystalline compound containing both nitrogen and sulphur, which was also obtained by the interaction of nitrogen sulphide and anisaldehyde, was easily separated from the other products by its insolubility in the ordinary solvents; it is readily soluble and stable in dilute solutions of the alkalis, and although the resulting salts could not be obtained in a state of purity from their aqueous or alcoholic solutions, yet the original substance was precipitated unchanged on neutralisation with acids. On the other hand, strong acids easily decompose the substance, when the whole of the sulphur present is eliminated as sulphur dioxide, while a part of the nitrogen is removed as ammonia and a good yield of anisoylanisamidine obtained. The composition of the latter substance was ascertained by its transformation into dianisamide on warming with dilute acids :



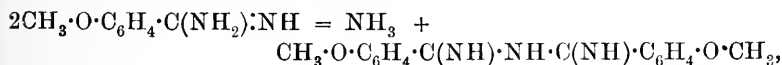
The formation of anisoylanisamidine suggested that, in all probability, the substance under investigation was an anisamidine derivative having the following constitution :



and that the action of acids on it is represented by the equation :



The imidic hydrogen atom in the amidines can be replaced by silver, as, for instance, silver benzamidine,  $\text{C}_6\text{H}_5\cdot\text{C}(\text{NH}_2):\text{NAg}$ . If the constitution of the substance in question is correctly indicated by the foregoing formula, its formation might be accounted for in the following manner. Firstly, two molecules of anisamidine lose ammonia:



and secondly, the resulting substance forms a closed ring with sulphur dioxide, the sulphur becoming attached to the imidic nitrogen atom as indicated in formula I.

#### EXPERIMENTAL.

The action of nitrogen sulphide on anisaldehyde was carried out at  $100^\circ$ , as previously described. Sulphur dioxide was evolved, and a rather better yield was obtained by the addition of either benzene or toluene towards the end of the reaction, because, after heating for some time, the mass became semi-solid, and consequently the reaction was completed very slowly unless one of these solvents be employed. It was found that 20 grams of nitrogen sulphide and about 50 grams of anisaldehyde gave 10 grams of tri-*p*-methoxyphenylecyanidine, 12 grams of anisamidine sulphate, 11 grams of the insoluble sulphur derivative, very much smaller quantities of free sulphur, and about 1 gram of ammonium sulphate. These substances are easily separated; first, by repeatedly washing with boiling benzene, which extracts the cyanidine derivative together with free sulphur, then by extracting the insoluble residue with a large quantity of boiling water, which dissolves out the anisamidine sulphate and the ammonium salt, leaving behind the third chief product as a colourless, crystalline powder.

I. *Tri-p-methoxyphenylecyanidine*.—When the benzene solution is allowed to cool, this substance, contaminated with small quantities of sulphur, separates out in small, white plates; it is easily purified by several crystallisations from benzene, and, as previously described, melts at  $217^\circ$ , dissolves only sparingly in alcohol, and, like the

majority of these cyanidine compounds, is stable at high temperatures; the following analytical data were obtained:  $C=72.47$ ;  $H=5.56$ ; whereas  $C_3N_3(C_6H_4 \cdot O \cdot CH_3)_3$  requires  $C=72.18$ ;  $H=5.26$  per cent. A molecular weight determination by the ebullioscopic method, using benzene as solvent, gave 422 and 437, the theoretical molecular weight being 399.

II. *Anisamidine Sulphate*.—When the aqueous solution of this salt is evaporated to about one-fourth of its bulk, large, well-formed, colourless prisms and pyramids separate out on cooling, leaving the ammonium sulphate in solution. This substance is insoluble in the ordinary organic solvents, is easily purified by recrystallisation from water, and melts above  $270^\circ$ ; the following results were obtained on analysis:  $C=48.50$ ;  $H=5.22$ ;  $N=14.4$ ;  $H_2SO_4=24.59$ ; whereas  $[CH_3 \cdot O \cdot C_6H_4 \cdot C(NH_2) : NH]_2, H_2SO_4$  requires  $C=48.24$ ;  $H=5.52$ ;  $N=14.06$ ;  $H_2SO_4=24.60$  per cent.

On double decomposition with barium chloride, the corresponding hydrochloride was obtained; this, on recrystallisation from alcohol, melted at  $217^\circ$  (Lossen, *Annalen*, 1897, 297, 385, gives the melting point as  $220^\circ$ ). On analysis, it gave  $HCl=19.0$ , whereas anisamidine hydrochloride,  $CH_3O \cdot C_6H_4 \cdot C(NH_2) : NH, HCl$ , requires  $HCl=19.5$  per cent.

The platinichloride, obtained by the addition of platinic chloride to an aqueous solution of the hydrochloride, crystallises well from water, and gave the following data on analysis:  $Pt=(I) 27.1$  and  $(II) 27.3$ ;  $(C_8H_9ON)_2, H_2PtCl_6$  requires  $Pt=27.4$  per cent.

The nitrate obtained from the sulphate by double decomposition with barium nitrate crystallises in long needles fusing at  $182-183^\circ$ , whereas Lossen gives  $181^\circ$ .

The properties of anisamidine and its salts have been described by Tafel and Enoch (*Ber.*, 1890, 23, 103) and by Lossen (*loc. cit.*). Briefly, it is a powerful base, having an alkaline reaction, but it is so easily decomposed by water that it is impossible to investigate its properties in solution. The sulphate, hydrochloride, and nitrate are neutral to litmus in aqueous solution. The molecular conductivity of solutions of the hydrochloride, determined by Mr. F. L. Usher, attain a maximum value at moderate dilutions, the salt behaving similarly to the chlorides of the alkali metals.

<i>v</i> litres .....	10	50	250	500	$\infty$
$\mu$ .....	87.8	101.0	109.0	112.2	113.0

Tafel and Enoch do not give the melting point of the free base, but Lossen states that it is  $112^\circ$ . We made several attempts to isolate anisamidine from the sulphate by rapidly treating a well-cooled solution of the latter with caustic potash and extracting with ether, but only

succeeded in obtaining a substance melting at  $119^{\circ}$ ; this product, which crystallises well from benzene, is readily and completely soluble in water, giving an intensely alkaline solution. The aqueous solution slowly deposits crystals of anisamide, a reaction which takes place immediately on warming. The anisamide thus obtained melted at  $165^{\circ}$ , whereas it is usually stated to fuse at  $163^{\circ}$ , but an analysis left no doubt as to its identity:  $C=63.26$ ;  $H=6.06$ ;  $N=9.80$ ;  $CH_3 \cdot O \cdot C_6H_4 \cdot CO \cdot NH_2$  requiring  $C=63.57$ ;  $H=5.96$ ;  $N=9.27$  per cent. Moreover, when heated with caustic alkalis and subsequently treated with acids, the amide gave anisic acid melting at  $181^{\circ}$ . Although our product had the properties and characteristics of anisamidine, yet analysis showed that it was far from pure. Several attempts were made to prepare the pure base by using its hydrochloride, as Tafel had done, instead of the sulphate, but without success; the resulting substance either melted at about  $119^{\circ}$  and contained about 3 per cent. less nitrogen than is required for anisamidine, or was so contaminated with anisamide that further purification was impossible.

III. The insoluble crystalline powder left on dissolving out the anisamidine sulphate melted and decomposed at  $200-205^{\circ}$ , and is only freed with difficulty from the last traces of the cyanidine compound by washing with large quantities of boiling benzene. It is only very slightly soluble in the ordinary organic solvents, but may be recrystallised from hot nitrobenzene, when it is obtained in small, well-formed plates fusing sharply and decomposing at  $205^{\circ}$ , the melting point remaining constant on recrystallisation from amyl alcohol.

The substance is readily soluble in dilute aqueous caustic potash or soda, and is precipitated unchanged from these solutions by acids and even by carbon dioxide. If concentrated solutions are employed, the substance is at once converted on warming into an oil which is not affected by prolonged boiling, but at once passes into solution on the addition of sufficient water. In the case of caustic potash, if the oil is separated, it slowly sets to a solid mass soluble in alcohol, which contains 14.4 per cent. of potassium, but as the substance could not be recrystallised or otherwise purified, this analytical result merely serves to indicate that we are dealing with the potassium salt of the original substance. This salt is readily soluble in water, and, although a neutral solution could not be obtained, it gave white precipitates with silver nitrate and with lead acetate, and a light blue one with copper sulphate. The silver salt was readily soluble in ammonia and on boiling separated out in masses resembling cotton-wool; the lead salt showed no signs of darkening on prolonged boiling. These results led to the conclusion that, in all probability, the metal was not attached to sulphur. Powerful reducing agents such as hydriodic

acid or phenylhydrazine liberate the sulphur as sulphuretted hydrogen. On gently warming with concentrated hydrochloric acid or, preferably, sulphuric acid, the whole of the sulphur was eliminated as sulphur dioxide, and when the solution was poured on to ice and neutralised with caustic soda, ammonia was evolved and anisoylanisamidine separated out as a white, crystalline mass; this product was soluble in the ordinary organic solvents, and when crystallised from benzene gave the following analytical data:  $C=67.32, 67.55$ ;  $H=6.03, 5.98$ ;  $N=10.26$ ;  $C_{16}H_{16}O_3N_2$  requires  $C=67.60$ ;  $H=5.63$ ;  $N=9.85$  per cent.

A methoxyl determination by Zeisel's method gave  $OCH_3=21.26$  per cent., the calculated value being  $21.83$  per cent.

A molecular weight determination by the ebullioscopic method, using benzene as solvent, gave 309 and 303, the theoretical molecular magnitude being 284.

The platinichloride, which separates slowly as a definitely crystalline substance on adding platinic chloride to a dilute solution of the base in acetone, water, and hydrochloric acid, is almost insoluble in water and alcohol and melts and decomposes at  $239^\circ$ .  $Pt=19.82$ ;  $(C_{16}H_{16}N_2O_3)_2, H_2PtCl_6$  requires  $Pt=19.86$  per cent.

That the substance was actually anisoylanisamidine was fully confirmed by dissolving it in dilute hydrochloric acid and heating for some time at  $70-80^\circ$ , when well-formed needles of dianisamide slowly separated. This product, which is preferably recrystallised from benzene, is moderately soluble in hot alcohol; it dissolves in caustic potash solution and is reprecipitated by acids. It melts at  $170^\circ$  and on analysis gave the following data:  $C=67.21$ ;  $H=5.49$ ;  $N=5.15$ ;  $(CH_3 \cdot O \cdot C_6H_4 \cdot CO)_2NH$  requires  $C=67.37$ ;  $H=5.26$ ;  $N=4.91$  per cent.

Having now proved that the insoluble substance, resulting from the interaction of nitrogen sulphide and anisaldehyde, gives rise to anisoylanisamidine on treatment with acids, and that the yield obtained,  $3.4$  from  $5$  grams, showed that it was the main product of the reaction, we considered that an important clue to the composition of the original compound had been obtained. We found that the analysis, which was again repeated, agrees fairly well, considering the difficulty experienced in the combustion, with a substance having the empirical formula  $C_{16}H_{16}N_3O_3S$ :  $C=59.12, 59.27$ ;  $H=5.09, 4.98$ ;  $N=12.72$ ;  $S=10.78, 10.51$ ;  $C_{16}H_{15}N_3O_3S$  requires  $C=58.35$ ;  $H=4.56$ ;  $N=12.76$ ;  $S=9.72$  per cent. An estimation of sulphur, liberated as sulphur dioxide on treating the substance with hydrochloric acid, gave  $S=9.42$  per cent.

A Zeisel determination of the methoxyl groups gave  $CH_3O=17.2$ , whereas the foregoing formula requires  $CH_3O=18.8$  per cent.; but the

determination was hardly expected to be accurate owing to the difficulty experienced with the sulphuretted hydrogen liberated by the hydriodic acid employed and to the fact that substances containing sulphur seldom give reliable data.

An analysis of the silver salt gave  $\text{Ag} = 23.58$ , the theoretical value for  $\text{C}_{16}\text{H}_{14}\text{O}_3\text{N}_3\text{SAg}$  being  $\text{Ag} = 24.77$  per cent. Unfortunately, owing to its insolubility, it was not found possible to determine its molecular magnitude. Although the foregoing analyses differ somewhat considerably from the calculated values, we think, however, they leave but little doubt that the substance has the empirical formula we have assigned to it, and that its stability towards alkalis, and especially the formation of anisoylanisamidine on treatment with acids, points clearly to the constitutional formula given on p. 1537.

We have made several attempts to obtain ethyl and benzoyl derivatives, but so far without success; we hope, however, to continue the investigation of this interesting substance.

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CLVI.—*Studies of Dynamic Isomerism. II. Solubility as a means of determining the Proportions of Dynamic Isomerides in Solution. Equilibrium between the Normal and Pseudo-Nitro-derivatives of Camphor.*

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THE method of studying dynamic isomerism described in the present communication, of which a preliminary account has already been given (Proc., 1903, 19, 156), is based on the determination of the gradual alteration in solubility which accompanies isomeric change. Although the measurements are somewhat troublesome to make and accurate results are not easily secured, the method is widely applicable; indeed, it can be used in all cases in which a sparingly soluble substance undergoes change with moderate velocity in solution. The method is most readily applied in the case of optically active substances, but can also be used when the isomerides are optically

inactive. The method has the unique advantage that it is possible from the measurements of initial and final solubility to deduce the proportions in which dynamic isomerides are in equilibrium in the solution even when only one of them can be isolated in the solid state.

The principle involved is briefly as follows. If a solid substance be stirred with a solvent at constant temperature, the amount dissolved will gradually increase until a steady state is reached and the solution is saturated. If, now, the dissolved substance should undergo change, a further quantity of the solid must dissolve in order to keep the solution saturated. The total weight of dissolved material will therefore be increased by an amount that will correspond with the extent to which the products of change have accumulated in the solution. If the change be reversible, this accumulation will ultimately stop the action; a steady state will then be reached in which there is equilibrium both between the different substances in solution and between one of the substances in the solution and the same substance in the solid state; the solution may then be again described as being saturated.

In the case of compounds which undergo reversible isomeric change in solution, the term "saturation" may be applied either to the transient condition of equilibrium which precedes isomeric change or to the stable equilibrium which follows it. The first type of saturation determines the *initial* or *true* solubility of the unchanged compound; the second type determines the *final* or *apparent* solubility. The ratio of the initial to the final solubility is equal to the ratio of the weight of the original substance to the total weight of material in solution. Thus, if the solubility increase in the ratio of 1 to 4, it may be assumed, at least as a first approximation, that the original substance forms one-fourth of the total matter in solution when equilibrium is established.

In tracing the course of isomeric change and determining the proportions in which dynamic isomerides are in equilibrium in solution by this method, certain difficulties are encountered.

(1) The determination from the ratio of the initial to the final solubility of the proportions in which the isomerides are present in solution depends on the assumption that the solubility of the original material is not influenced by the products of isomeric change. This assumption is only strictly valid in the case of "dilute solutions" in which these products are present in very small proportions; by selecting solvents in which the original solid is sparingly soluble and by working at a low temperature, this source of error may be reduced to any desired extent. Even in more concentrated solutions, containing 5 or 10 per cent. of solid, the effects produced are not necessarily very serious; their magnitude may be estimated by making

experiments directly with substances similar in constitution to the actual products of change.

(2) The determination of the final solubility usually presents no special difficulty beyond that involved in maintaining a constant temperature during a period of 2 or 3 weeks. But in certain instances, in which the solute is liable to decompose or the composition of the solvent to alter by evaporation of the lighter fractions, it may be necessary to hasten the attainment of equilibrium by the addition of a trace of some catalyst. In determining the initial solubility, difficulties are only encountered when isomeric change is rapid. In this case, it is not easy to effect saturation of the solution before the increased solubility consequent on isomeric change has begun to make itself felt. For this reason it is necessary to secure conditions under which saturation shall be effected rapidly and isomeric change slowly. The former condition is secured by vigorous stirring and by using the solid in a finely powdered condition; it is then usually possible to ensure that saturation is substantially complete within 5 or 10 minutes. In other cases, when the solution is viscous or when the solubility is so great that all the finest particles are dissolved before the solution is saturated, half an hour or more must be allowed. The second condition is secured by using inactive solvents, such as benzene, chloroform, or light petroleum, rather than ionising solvents, such as water or alcohol, as well as by making the measurements at the lowest temperature that is available. But even when these precautions are taken, there are still many instances in which isomeric change occurs so rapidly that it is not possible to determine accurately the initial solubility of the unchanged substance. In this respect, the method will not compare with the observation of optical rotatory power, as a change of rotatory power can be detected even if it take place so rapidly as to be complete within 10 minutes. The time occupied in detecting a change of solubility is at least an hour, being considerably longer if the initial solubility is to be accurately determined.

(3) In preparing materials for solubility measurements, much care must be taken to ensure that the solid shall consist entirely of the one isomeride. As the conditions governing the crystallisation of dynamic isomerides have already been discussed (*Trans.*, 1899, 75, 231), it will be sufficient to refer to the fact that rapid crystallisation almost invariably yields a mixture of isomerides, but that this mixture may be rendered homogeneous by soaking the powdered mass of crystals with a solvent until the whole of the labile solid has passed into solution and separated (after undergoing isomeric change) in the stable form. The best test of homogeneity is to extract the sample at constant temperature with successive small quantities of a solvent. If two successive solubility determinations give the same value, the material

may usually be regarded as being uniform, although a mixture of isomerides would also give concordant figures if the labile form were present in sufficient quantity to make it possible to saturate the solution with regard to both isomerides.

(4) In the preceding discussion, it has been assumed that the solid used in effecting saturation is that which is stable in contact with the solvent, although it is not necessarily the major constituent of the solution. The behaviour of the labile isomeride may now be briefly described. As in the case of the stable isomeride, the initial state of saturation is followed by an increase of solubility consequent on the occurrence of isomeric change. But before the dissolved isomerides are in equilibrium, the solution becomes saturated with regard to the stable isomeride, which then begins to separate in the solid state: being saturated with regard to both isomerides, the solution appears to have reached a steady condition, the solubility remaining constant during a considerable period of time. But although the composition of the solution remains apparently constant, isomeric change proceeds continuously, the labile form gradually dissolving, whilst an equal quantity of the stable form separates from the solution. Ultimately the supply of the labile isomeride becomes exhausted and it is no longer able to saturate the solution. But as the proportion in solution is still in excess of that in which the isomerides are in equilibrium with one another, isomeric change continues. A further separation of the stable isomeride then takes place, but this is now accompanied by a decrease in the concentration of the solution. This change in concentration ceases when a condition of equilibrium is reached identical with that effected by prolonged contact of the solvent with the stable isomeride, as described in the preceding paragraphs.

*Form of the Curves.*—The ordinary mutarotation curves expressing the change of rotatory power with time are logarithmic in form and depend on the sum of the velocity constants of isomeric change in the two directions, thus:

$$\frac{1}{t} \log \frac{x_0 - x_\infty}{x_t - x_\infty} = k_1 + k_2,$$

where  $t$  is the time,  $k_1$  and  $k_2$  are the velocity constants, and  $x_0$ ,  $x_\infty$ ,  $x_t$  are the rotatory powers, initially, finally, and at time  $t$  (Trans., 1899, 75, 225). The increase of solubility with time is given by the equation:

$$\frac{dx}{dt} = k_1 x_0 - k_2 (x_t - x_0),$$

which, when integrated, becomes

$$\frac{1}{t} \log \frac{k_1 x_0}{+ k_2 x_0 - k_2 x} = k_2,$$

$$\text{or since } \frac{k_1 + k_2}{k_2} = \frac{x_\infty}{x_0},$$

$$\frac{1}{t} \log \frac{x_\infty - x_0}{x_\infty - x_t} = k_2^*,$$

where  $x$  may be either the solubility (weight of solute in unit weight or volume of solvent or solution) at time 0,  $t$  and  $\infty$ , or the initial or final rotatory power of samples of the saturated solution taken at times 0,  $t$  and  $\infty$ .

In the simplest case, in which only two isomerides are in equilibrium in solution, the solubility curves are, therefore, logarithmic in form, like the mutarotation curves. But whilst the mutarotation curves are determined by the sum of the velocities of isomeric change in opposite directions, the solubility curves are dependent on the velocity of isomeric change in one direction only. It is not a little remarkable that, although the increase of solubility is due to the conversion of the "stable" into the "labile" isomeride, the velocity of this direct isomeric change does not enter into the equation, which includes only the velocity constant of the reversed isomeric change or back action by which the labile is reconverted into the stable isomeride.

In the present communication, the results are recorded of experiments which were made in order to determine the proportions in which the normal and pseudo-forms are in equilibrium in solutions of nitrocamphor,  $\pi$ -bromonitrocamphor and  $\beta$ -bromonitrocamphor. The method adopted was that used in the investigation of glucose and galactose; it is described in detail in the following paper.

1. *Nitrocamphor*.—The changes of rotatory power which take place in freshly-prepared solutions of nitrocamphor have been fully investigated (Trans., 1899, 75, 215). The pseudo-form of nitrocamphor has not yet been isolated; a comparison of the rotatory powers of a number of its derivatives shows, however, that this substance may be expected to have a high dextrorotatory power. On the assumption that  $[\alpha]_D$  is about  $+180^\circ$ , the proportion of the pseudo-form when equilibrium is attained in solution would appear to be about 7 per cent.; the experiments described below show, however, that the proportion is considerably greater.

As the stable (normal) form of nitrocamphor is also the major constituent in solution, no difficulty is experienced in preparing it free from the labile pseudo-form. Although the crystals that separate from alcohol

\* This equation is identical in form with that for the hydrolysis of a lactone, which has been worked out by C. S. Hudson (*Zeit. physikal. Chem.*, 1903, 44, 487—494).

were practically pure, as an additional precaution they were soaked in light petroleum before being used. On account of the excessive solubility of nitrocamphor in benzene and chloroform, neither of these liquids could be used as a solvent; moreover, alcohol was unsuitable on account of the great rapidity with which isomeric change took place in it. Light petroleum seemed to be the only suitable solvent; two samples were tested, the one boiling at 60–80°, the other at 85–100°. The more volatile fraction was unsuitable, because an inconveniently small amount of nitrocamphor was dissolved by it and also because solutions were obtained which, in the course of a week, exhibited neither mutarotation nor an increase of solubility; the less volatile fraction gave satisfactory results.

It was not possible to determine the concentration of the saturated solutions by evaporating, as the nitrocamphor began either to decompose or to sublime before the whole of the petroleum was removed, so that constant weights could not be obtained. The solutions were therefore kept until the rotatory power was constant; the final rotatory power was taken as a measure of the weight of nitrocamphor in solution. Altogether seven series of observations were made. From four of these, it was possible to deduce the ratio of the initial to the final solubility. The experimental data summarised in Table I give for this ratio the values 0.85, 0.79, 0.83 and 0.81; mean, 0.82. It may therefore be concluded that equilibrium is reached when 82 per cent. of the nitrocamphor is in the normal and 18 per cent. in the pseudo-form. The ratio of normal to pseudo is thus nearly 5 : 1.

TABLE I.—*Rotatory Power of Saturated Solutions of Nitrocamphor in Light Petroleum at 20°.*

I. Initial [ $-110'$ ] $\frac{1}{2}$ hour 111 1 " 112 3.5 hours 126 6 " 129 8.5 " 129 27 " 127	II. Initial [ $-100'$ ] 1.2 hours 104 3 " 111 5 " 125 24 " 126
Ratio 110/129 = 0.85	Ratio 100/126 = 0.79
III. Initial [ $-105'$ ] 1 hour 106 2 hours 107 6.2 " 112 24 " 127	IV. Initial [ $-83'$ ] 1 hour 89 2.1 hours 96 24 " 103 2 days 103
Ratio 105/127 = 0.83	Ratio 83/103 = 0.81

The angles given are the steady values observed in 2-dcm. tubes at 20°.

2.  *$\pi$ -Bromonitrocamphor*.—Both the normal and the pseudo-form of this substance have been isolated (Lapworth and Kipping, Trans., 1896, 69, 304; Lowry, Trans., 1899, 75, 223). Although the minor constituent in solution, the pseudo-form separates first on crystallisation and is therefore the stable isomeride. The labile normal form can, however, be separated by rapidly evaporating a solution in chloroform, when crystals of both forms separate from the solution sufficiently large to be picked out by hand. In this way, samples of the normal form can be obtained which exhibit in solution a change of rotatory power from left to right; that is, in the same direction as that which occurs in the case of nitrocamphor but in a direction opposite to that which is observed in solutions of the pseudo-form of  $\pi$ -bromonitrocamphor. The pseudo-form has a specific rotatory power  $[\alpha]_D + 188^\circ$  in benzene; the best sample obtained of the normal form gave  $[\alpha]_D - 51^\circ$ ; when equilibrium is attained, solutions prepared from either form give  $[\alpha]_D - 38^\circ$ . From these figures, it may be deduced that the normal and pseudo-forms are in equilibrium in the proportion of 226 : 13, that is, when 6 per cent. of the solute is present in the pseudo-form. The value  $[\alpha]_D - 51^\circ$  for the normal form can, however, be regarded only as a minimum value, as it is probable that even the best samples contained a little of the stable pseudo-isomeride; the actual proportion of the pseudo-form is probably much greater than that indicated above.

In the experiments with  $\pi$ -bromonitrocamphor, the solvent used was a mixture of equal volumes of purified benzene and light petroleum. As the rotatory powers of the saturated solutions were too small to give accurate results, the concentrations were determined by evaporating known weights of the saturated solutions. The ratio of the initial to the final solubility deduced from the weights of solute per 100 grams of solution was  $1.00/5.76 = 0.17$ , whilst the approximate value deduced from the rotatory powers was  $-11' / -53' = 0.21$ . The former value is the more trustworthy and shows that, as in the case of nitrocamphor, the ratio of the normal and pseudo-forms is approximately 5 : 1.

This result is of interest in view of the fact that the normal form is the first to separate from solutions of nitrocamphor, whilst in the case of the  $\pi$ -bromo-derivative the pseudo-form separates first. As the proportions are substantially the same in the two cases, it would appear that the bromine atom has no marked influence in determining the ratio in which the two forms are in equilibrium in solution. The stability, in contact with the solvent, of the normal form of nitrocamphor but of the pseudo-form of its  $\pi$ -bromo-derivative must therefore be ascribed wholly to an alteration in the relative solubility, not in the relative proportions of the normal and pseudo-forms.

3.  *$\beta$ -Bromonitrocamphor*.—This substance resembles  $\pi$ -bromonitro-

camphor in that the pseudo-form is stable (Lowry, Trans., 1903, 83, 965). It has not been found possible to separate the normal form and nothing was known as to the relative proportions of the two substances in solution. Whilst  $\pi$ -bromopseudonitrocamphor is very strongly dextrorotatory, the  $\beta$ -compound is almost inactive; the purest specimens obtained were feebly dextrorotatory when dissolved in benzene; solutions in chloroform showed a larger initial dextrorotatory power. The gradual change of rotatory power of solutions of  $\beta$ -bromonitrocamphor (crystallised from acetic acid and dissolved in benzene and chloroform) is shown in Table II and in Figure 1 (p. 1549).

TABLE II.—*Mutarotation of  $\beta$ -Bromopseudonitrocamphor in Benzene and Chloroform.*

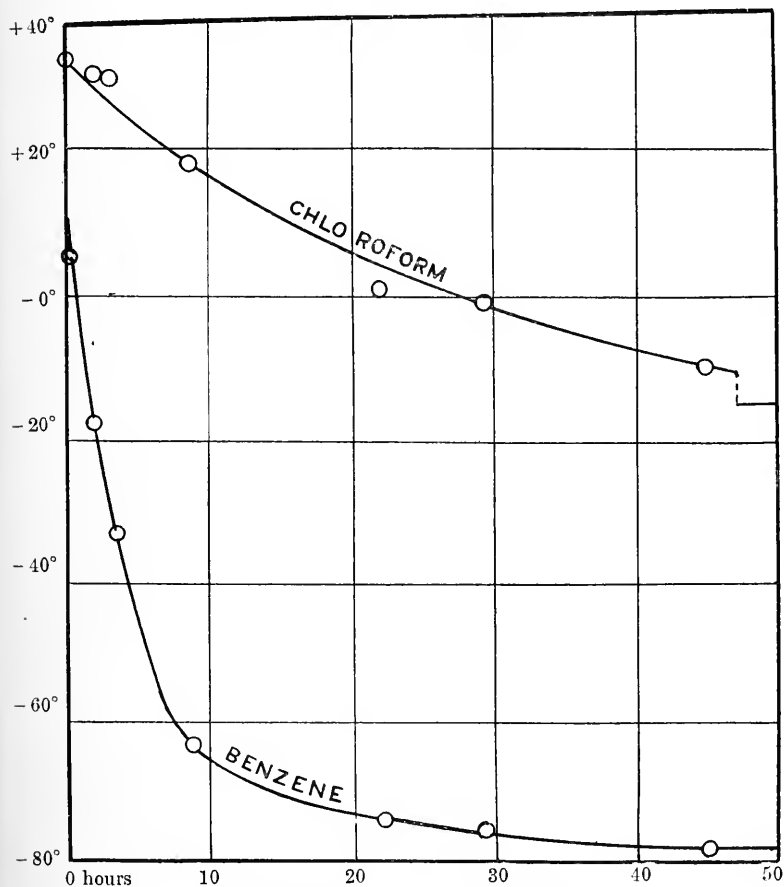
(a) Benzene.			(b) Chloroform.		
Time.	$[\alpha]_D$ .	Temp.	Time.	$[\alpha]_D$ .	Temp.
10 m.	+ 5.8°	15°	10 m.	+32.9°	15°
1 h. 50 m.	-18.8	"	1 h. 50 m.	+30.8	"
3 h. 20 m.	-32.9	"	3 h. 5 m.	+30.0	"
8 h. 55 m.	-63.3	"	8 h. 55 m.	+18.3	"
22 h. 0 m.	-74.2	17	21 h. 50 m.	+ 1.2	17
29 h. 15 m.	-75.8	"	29 h. 15 m.	- 0.8	"
45 h. 10 m.	-78.3	"	45 h. 0 m.	- 9.2	"
5 days.	-76.7	22	5 days.	- 15	22

The final specific rotatory power of a solution in benzene decreases rapidly as the temperature rises; the decrease amounts to approximately 1° per degree Centigrade.

Two series of experiments were carried out in order to determine the ratio of the initial to the final solubility of  $\beta$ -bromonitrocamphor. In the first of these, the solvent was merely shaken at atmospheric temperature (9°) with the finely-powdered crystals and then filtered and evaporated. The solubility in benzene was thus found to increase in the ratio of 2.3 to 9.2 grams per 100 grams of benzene (Proc., 1903, 19, 157); although this value can only be regarded as an approximation, it clearly indicates that the proportions of the normal and pseudo-forms do not differ substantially from those observed in the case of nitrocamphor and its  $\pi$ -bromo-derivative. Subsequently, an attempt was made to determine the increment of solubility at 20° in a mixture of benzene and light petroleum, using the final rotatory powers of the samples as a measure of the weight of the dissolved substance. The initial experiments had to be rejected, as it was found that the solid

contained the normal as well as the pseudo-form. In two later experiments, however, the purity of the material was shown not only by the fact that two successive experiments gave concordant results but also

FIG. 1.



*Mutarotation of  $\beta$ -bromonitrocamphor.*

by the fact that the freshly-prepared solutions of the pseudo-form were dextrorotatory, though the sign of the rotation was soon reversed. The final rotatory powers of the saturated solutions in two experiments are shown in Table III.

TABLE III.—*Final Rotatory Power of Saturated Solutions of  $\beta$ -Bromonitrocamphor in a Mixture of Benzene and Light Petroleum at 20°.*

(a) $\frac{1}{2}$ hour	- 30'	(b) 1 hour	- 42'
1 „	- 42'	2 hours	- 74'
		3 „	- 93'
		5 „	- 127'
		9 „	- 169'
		29 „	- 190'
		2 days	- 232'
		3 „	- 232'

The values given in this table are concordant; when plotted graphically, the two series of observations fall together on a smooth curve. But the rotatory power deduced by extrapolation for zero time is only 16', giving as the ratio of initial to final solubility a value as low as 0.07. This abnormal result is probably due to the great velocity of isomeric change, which was approximately 10 times as rapid as in the case recorded in Table II. Under these conditions, the error due to extrapolation is greatly increased and no reliance can be placed on the value deduced for the initial solubility. The earlier experiments made at 9° indicate, however, sufficiently clearly that no marked difference is to be anticipated between the ratios of the normal to the pseudo-forms in the case of  $\beta$  bromonitrocamphor and the other two members of the group.

#### *Summary.*

The experiments now described afford the first example of the investigation of reversible isomeric change by means of solubility measurements and serve to show that the method is a practical one.

In the present paper, it is applied to the nitro-derivatives of camphor. The mutarotation of these substances had already been investigated but the proportions in which the isomerides were in equilibrium were not known. It is now shown that in the case of nitrocamphor and its  $\pi$ -bromo-derivative the normal and pseudo-forms are in equilibrium when present in the ratio 5 : 1 approximately.

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CLVII.—*Studies of Dynamic Isomerism. III. Solubility as a means of Determining the Proportions of Dynamic Isomerides in Solution. Equilibrium in Solutions of Glucose and of Galactose.*

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THE recent investigations of E. F. Armstrong (*Trans.*, 1903, 83, 1305; this vol., p. 1043) and of Behrend and Roth (*Annalen*, 1904, 331, 359) have established the fact that glucose exists in stereoisomeric forms corresponding with the  $\alpha$ - and  $\beta$ -glucosides.\* There can, therefore, be little doubt that the property of mutarotation in the case of this sugar, as in that of the nitro-derivatives of camphor, is closely associated with a reversible isomeric change by which the two forms of the substance are converted into one another. The equilibrium between the stereoisomeric glucoses may provisionally be represented by the scheme:



Although the constitution of the mutarotatory  $\alpha$ - and  $\beta$ -forms of glucose has been definitely determined, little is known either as to the proportions in which they are in equilibrium in solution or as to the mechanism by which isomeric change is brought about. The experimental part of this communication deals mainly with the first of these problems; the second is discussed at the close of the paper.

*Equilibrium between  $\alpha$ - and  $\beta$ -Glucoses.*

The specific rotatory power of  $\alpha$ -glucose is about  $109^\circ$  and that of  $\beta$ -glucose is about  $19^\circ$ ; the latter value is somewhat uncertain, as it is doubtful whether the specimens examined were free from the  $\alpha$ -isomeride. The rotatory power finally arrived at in aqueous solutions of either isomeride is  $[\alpha]_D + 53^\circ$ ; if no other substances but  $\alpha$ - and  $\beta$ -glucoses were present it would be possible to calculate directly the proportions of the two isomerides in the solution. But this method,

\* In the present paper, the terms  $\alpha$ - and  $\beta$ -glucose are used to describe the sugars from which the  $\alpha$ - and  $\beta$ -glucosides are derived. It is hoped that this systematic nomenclature will now be generally adopted in place of the terms provisionally introduced by Tanret at a time when the constitution of these sugars was unknown.

which would give the ratio of  $\alpha$ - to  $\beta$ -glucose as 3:5, is entirely vitiated if it be allowed that other substances, such as the aldehydic form of the sugar, may also be present in the aqueous solution; in fact it is impossible at present to draw any definite conclusions from the data afforded by the rotatory power of the solutions.

The behaviour of galactose is very similar to that of glucose. In a freshly prepared aqueous solution of  $\alpha$ -galactose,  $[\alpha]_D +140^\circ$ ; when the different forms of galactose are in equilibrium in solution, this value falls to  $+80^\circ$ . The low rotatory form corresponding with  $\beta$ -glucose has  $[\alpha]_D +53^\circ$ .

(1) In applying the method described in the foregoing paper to the mutarotatory sugars, the solubility was in all cases deduced from the rotatory power finally attained to in the samples of the saturated solutions drawn off from time to time. It was assumed that the rotatory power was directly proportional to the concentration of the solution; in other words, that the specific rotatory power of the sugar was constant within the narrow range of concentrations used in the experiments. This method of determining the concentrations was found to be very convenient except in the case of the most dilute solutions. It had the further advantage that both the initial rotatory power and the rate at which the steady rotatory power was attained were easily observed; the value of these additional observations is indicated later on.

(2) On account of the small rotatory power of the saturated solutions, ethyl alcohol could not be used as a solvent, whilst water was out of the question on account of the excessive solubility of the sugars. Suitable solvents were found in methyl alcohol and various mixtures of alcohol and water. In these solvents, isomeric change took place much more slowly than in water, several days or hours elapsing before the solubility reached a constant value. By means of a spiral stirrer driven by a small water-motor, the mixture of sugar and solvent was kept vigorously stirred, whilst a constant temperature was maintained by means of a water-bath fitted with a sensitive gas regulator. Under these conditions, saturation was usually complete within half an hour; there was therefore no difficulty in determining the initial solubility of the sugar but some patience was required in determining the final solubility, which, in the case of the methyl-alcoholic solutions, was not reached until more than a week had elapsed.

(3) In the early stages of the investigation, considerable difficulty was encountered in securing suitable material. Both glucose and galactose are readily purified by crystallising them from dilute methyl alcohol but the product is almost invariably a mixture of the different forms of the sugar. To obtain a homogeneous substance, the mixture was soaked during several days or weeks with anhydrous or aqueous

alcohol, either at 20° or at some higher temperature, until the whole of the  $\beta$ -sugar present had been converted into the  $\alpha$ -isomeride. The purity of the material was then tested by digesting the solid at constant temperature during periods of one hour with successive quantities of a solvent. If successive extracts showed the same rotatory power, the solid was regarded as homogeneous. In some cases it was possible to make two complete series of observations with the same sample of solid. In this case, the prolonged extraction during the first experiment was a sufficient guarantee of the uniformity of the solid in the second experiment; observations made in this way were, therefore, regarded as of exceptional value.

(4) In deducing from the ratio of the initial to the final solubility the proportion of the  $\alpha$ -sugar that is present in equilibrium in solution, it was of great importance to determine to what extent the solubility of the  $\alpha$ -sugar might be influenced by the presence in the solution of the  $\beta$ -sugar and other products of change. When methyl alcohol was used as the solvent, the errors due to this cause were likely to be small, as the solubility of  $\alpha$ -glucose at 20° ranges only from 1.0 to 1.9 grams per 100 c.c. and that of  $\alpha$ -galactose from about 0.2 to 0.4 gram. It can scarcely be supposed that the presence in the methyl alcohol of 0.9 per cent. of  $\beta$ -glucose or 0.2 per cent. of  $\beta$ -galactose would very appreciably affect the solubility of the  $\alpha$ -sugar, although this assumption would not be justified in the case of the more concentrated aqueous-alcoholic solutions. A direct experiment on the influence of the  $\beta$ -sugar on the solubility of the  $\alpha$ -sugar was not practicable but a very satisfactory test could be made by measuring the influence of  $\alpha$ - and  $\beta$ -glucoses on the solubility of  $\alpha$ -galactose or conversely. The solubility of  $\alpha$ -galactose was therefore determined (1) in a mixture of alcohol and water having approximately the composition represented by the formula  $\text{EtOH} + \text{H}_2\text{O}$  and (2) in a similar mixture containing 5 grams of glucose in 100 c.c. In the first case, after stirring during one hour with  $\alpha$ -galactose at 20°, the rotatory power of the saturated solution was  $\alpha_D = 2.4'$  in a 2-dm. tube. In the second case, the rotatory power of the solution was increased from  $5.55'$  to  $8.1'$ , a difference of  $2.6'$ . The two values for the rotatory power of a saturated solution of  $\alpha$ -galactose differ only by  $2'$ , a quantity that falls within the limits of experimental error; it is evident, therefore, that the presence in the solvent of 5 per cent. of glucose does not produce any measurable alteration in the solubility of galactose. In all the measurements described below, the products of change were present to the extent of less than 5 grams per 100 c.c.; their influence on the solubility of the  $\alpha$ -sugar may safely be neglected in view of the evidence afforded by the experiment just described.

*Solubility of Glucose in Methyl Alcohol.*

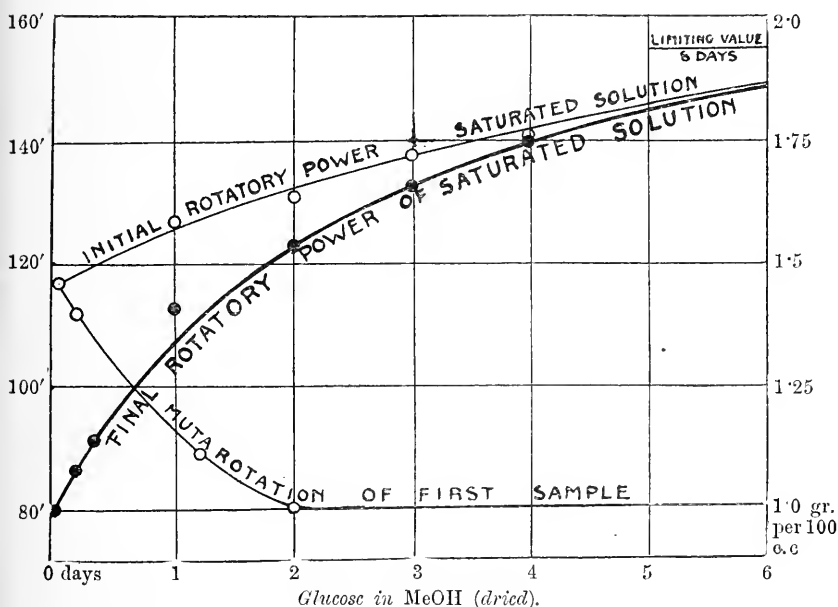
The first series of experiments was on the solubility of glucose in methyl alcohol at 20°. By a fortunate accident, the first crop of glucose consisted entirely of the  $\alpha$ -form, and gave concordant values when extracted with successive quantities of methyl alcohol. In these experiments, the samples were merely drawn off in a pipette and filtered quickly through a fluted filter into a polarimeter tube. Although this method of sampling is subject to error on account of evaporation and changes of temperature during filtration, the two series of observations with undried methyl alcohol gave very concordant results, whilst with alcohol dried by means of quicklime the change of solubility with time was precisely similar but slightly slower. The concentration of the solutions was determined from the final rotatory power of the samples observed two or three days subsequently to filtration; usually an observation was also made of the initial rotatory power of the sample immediately after filtration; in the case of the earlier samples, intermediate observations were made by means of which the velocity of the mutarotation could be determined. In the series of observations on the solubility of  $\alpha$ -glucose in dried methyl alcohol recorded in Table I and shown graphically in Fig. 1, the initial rotatory power of the first sample, taken after stirring during one hour, was  $\alpha_D + 117'$  in a 2 dm. tube, decreasing in the course of two days to  $\alpha_D + 80'$ ; this solution was found to contain 1 gram of glucose in 100 c.c. of solution.\* The gradual decrease in the rotatory power of this sample is shown by the mutarotation curve of Fig. 1 (p. 1555); the initial and final values are plotted as single points (with abscissæ corresponding with one hour) on the ascending curves of "initial" and "final" rotatory power of the saturated solutions.

In the later samples the change of rotatory power was less than in the first sample and at the end of a week the constituents of the solution were so nearly in equilibrium that there was little or no change of rotatory power subsequent to filtration. Ultimately, the rotatory power, which had been increasing continuously during this period, became constant at 155', a value which corresponds with a concentration of 1.9 grams of glucose in 100 c.c. The products of change had therefore accumulated to the extent of 0.9 gram in 100 c.c. before they were in equilibrium with the 1.0 gram of  $\alpha$ -glucose initially present in the solution. The proportion of  $\alpha$ -glucose when equilibrium is reached is 80/155 or 1.0/1.9 or 52 per cent. of the total weight of sugar in solution.

\* A solution prepared by dissolving a weighed quantity of glucose in methyl alcohol and diluting to 1.00 gram per 100 c.c. gave  $\alpha_D + 80'$ , agreeing exactly with the value for the steady rotatory power of the first sample.

In the case of the methyl-alcoholic solutions, there is reason to think that mutarotation is almost wholly due to isomeric change and that the increase of solubility affords a direct measure of the amount of  $\beta$ -glucose present in the solution. On this assumption, it is possible to calculate from the foregoing data the specific rotatory power in methyl-alcoholic solution of  $\alpha$ - and  $\beta$ -glucoses and of the mixture which is formed from these sugars in solution. A 1 per cent. solution of  $\alpha$ -glucose gave  $\alpha_D + 117'$  in a 2-dcm. tube; therefore  $[\alpha]_D = 98^\circ$ . The presence of 0.9 per cent. of  $\beta$ -glucose raised the rotatory power

FIG. 1.



from  $117'$  to  $155'$ ; therefore  $[\alpha]_D = 35^\circ$ . A 1 per cent. solution of the mixture gave  $\alpha_D + 80'$ ; therefore  $[\alpha]_D = 67^\circ$ .

The rotatory power of the glucoses in methyl alcohol may be compared with the values in aqueous solution and with those for the corresponding glucosides.

	$\alpha$ .	$\beta$ .	Mean.	$\alpha \rightleftharpoons \beta$ .
Glucose in methyl alcohol.....	+ 98°	+ 35°	+ 66°	+ 67°
Glucose in water .....	109	< 19	64	53
Methylglucoside in water .....	158	- 32	63	—
Ethylglucoside in water .....	151	- 30	60	—

It will be noticed that, although there is a wide variation in the

values for the different compounds, the mean values are almost identical for each pair of stereoisomerides. The variations of rotatory power are therefore to be attributed to changes in the asymmetry of the terminal carbon atom, whilst the configuration of the rest of the molecule is so far constant that the four remaining asymmetric carbon atoms have the same optical properties in each of the compounds under consideration.

TABLE I.—*Glucose in Methyl Alcohol at 2.0°.*

I.			II.			III.		
Time.	$\alpha_D$ . Initial.	$\alpha_D$ . Final.	Time.	$\alpha_D$ . Initial.	$\alpha_D$ . Final.	Time.	$\alpha_D$ . Initial.	$\alpha_D$ . Final.
0.5 h.	114'	[80']	0.5 h.	122'	81'	0.5 h.	—	80'
3 h.	114'	85'	1 h.	122'	81'	1 h.	117'	80'
6 h.	116'	90'	4 h.	127'	90'	4 h.	—	86'
12 h.	120'	97'	10 h.	129'	94'	8 h.	—	91
31 h.	126'	115'	25 h.	129'	114'	24 h.	127'	113'
48 h.	132'	127'	48 h.	136'	127'	48 h.	131'	123'
54 h.		133'	54 h.	138'	133'	72 h.	138'	133'
6 days		148'	10 d.		149'	96 h.	141'	140'
7 days		148'	16 d.		148'	8 d.		156'
22 days		154'	21 d.		149'	11 d.		155'
27 days		156' f	23 d.		151'	16 d.		151'
						18 d.		159'

Ratio 80'/155' = 52%

Ratio 81'/149' = 54%

Ratio 80'/155' = 52%

In the third series, the solvent had been dried by distilling from quicklime; this produced a very slight decrease in the rate of change but did not alter the ratio of the initial to the final solubility.

The observed rotatory powers,  $\alpha_D$ , refer in all cases to 2-dcm. tubes. A solution containing 1 gram of glucose in 100 c.c. gave  $\alpha_D = 80'$ .

### *Solubility of Galactose in Methyl Alcohol.*

The observations show that in methyl-alcoholic solution the two stereoisomeric glucoses are present in approximately equal proportions; they may therefore be regarded as almost equally stable. It was of interest to extend the observations to another sugar in order to ascertain whether the equal stability of the stereoisomerides was a peculiar property of glucose or a general characteristic of the aldoses. The sugar chosen for investigation was galactose, which differs from glucose only in the altered configuration of the groups attached to the fourth carbon atom. Like glucose, galactose is very readily purified by crystallising from aqueous methyl alcohol; by adopting the usual precautions a specimen was obtained which consisted wholly of the  $\alpha$ -form. The solubility of galactose in methyl alcohol is even less than that of glucose; only the initial and final values were determined. Two solutions, prepared by stirring  $\alpha$ -galactose with methyl alcohol during one hour at 20°, were filtered and kept until the rotatory power

became constant at  $\alpha_D + 17'$ . Two other solutions were prepared by keeping the solvent in contact with the solid during several weeks at  $20^\circ$ ; these gave  $\alpha_D + 34'$ . The ratio of the initial to the final solubility is therefore 17:34 or 1:2, showing that, as in the case of glucose, the two stereoisomerides must be present in equal quantities and be equally stable in solution. This result is of interest as indicating that the relative stability of the  $\alpha$ - and  $\beta$ -forms of the sugars is not influenced even by the important difference of configuration which distinguishes glucose from galactose.

### *Solubility in Mixtures of Alcohol and Water.*

The foregoing measurements were rendered difficult by the slight solubility of glucose and galactose in methyl alcohol. In the later experiments, mixtures of alcohol and water were used; by varying the proportions, it was possible to increase or decrease the solubility of the sugar at will. These experiments had the further advantage that the conditions approximated much more nearly to those obtaining in aqueous solution and although the proportion of water could not be increased beyond 50 per cent. on account of the excessive solubility of the sugars, it was nevertheless possible to obtain some idea of the conditions which prevail when the sugars are dissolved in water.

The regulation of temperature had by this time been greatly improved and the variations in the temperature of the thermostat used in preparing the saturated solutions had been reduced from a tenth to one or two hundredths of a degree. The polarimeter had also been provided with a copper jacket in which the tubes under observation could be kept at  $20^\circ$  by means of a stream of water heated by an automatically regulated gas flame. The temperature-coefficient for these sugars is so small that no difference could be detected in the rotatory powers at  $20^\circ$  and at atmospheric temperatures; but, as the polarimeter tubes were filled at  $20^\circ$ , it was found that the solutions were much more transparent when kept at this temperature than when, before reading the initial rotatory power, the temperature was allowed to fall; in the latter case, the formation of layers of unequal density increased the opacity of the liquid and rendered the earlier readings somewhat untrustworthy.

A further improvement was also effected in the method of taking the samples. The methyl-alcoholic solutions were so mobile that the errors caused by cooling and evaporation in filtering were not serious. The aqueous-alcoholic solutions were, however, very viscous, filtering so slowly that it was necessary to adopt a new method of filtration. Meyerhoffer-Saunders' pipette could not be used as it was impossible to secure uniform packing of the asbestos or cotton-wool which fills the

filtration-bulb. Excellent results were obtained by using tubes of the form shown in the accompanying figure.

FIG. 2.

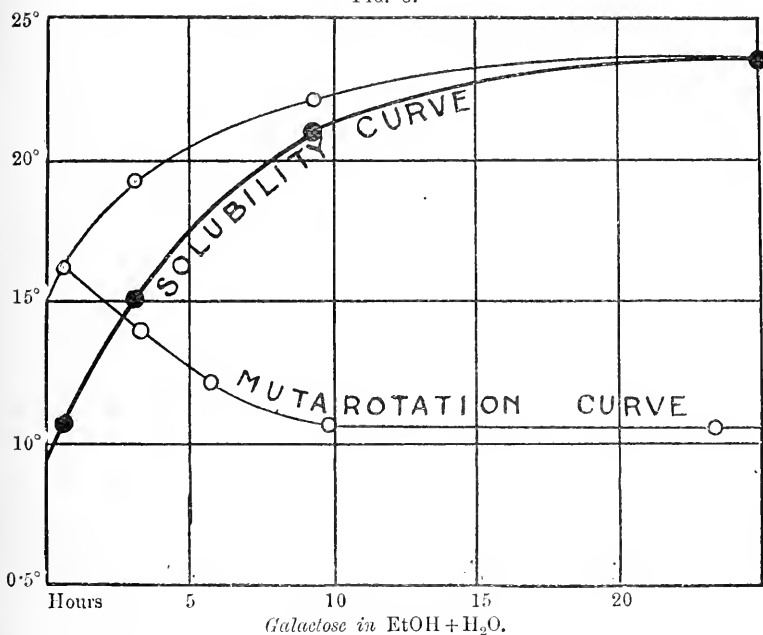


The wide end of the tube was covered with two layers of filter-paper of suitable density and a layer of linen held in place by an india-rubber band. The tube was first heated to  $20^{\circ}$  in a test-tube plunged into the water-bath, and was then lowered into the saturated solution and a sample was drawn up through the filter-paper. This was transferred by simply inverting the filtration tube into a polarimeter tube which had also been heated to  $20^{\circ}$ . The polarimeter tube was then placed in the copper jacket of the polarimeter and kept at  $20^{\circ}$  whilst under observation. By this means, the ease and accuracy of working were greatly increased and the method was substantially perfected; but as the changes studied were more rapid and more complex than in the methyl-alcoholic solutions the results obtained were of approximately equal value. The curves are to be regarded rather as showing the general trend of the action than as affording exact data for the application of the laws of mass-action.

#### *Solubility of Galactose in Aqueous Alcohol.*

The measurements of the solubility of glucose in aqueous alcohol were complicated by the formation of a crystalline hydrate. The observations with galactose were not so affected; and owing to the smaller solubility of galactose, it was possible to make measurements with solvents containing nearly 50 per cent. of water. The mixtures used were made by diluting known weights of dried alcohol and had approximately the compositions represented by the formulæ  $C_2H_6O + H_2O$ ,  $C_2H_6O + 2H_2O$ ,  $C_3H_8O + 2H_2O$ . The results obtained are shown in Table II; one series of observations is plotted graphically in Fig. 3 (p. 1559). It will be noticed that in the aqueous-alcoholic solutions the ratio of the initial to the final solubility is much less than 50 per cent.; it decreases to 39 per cent. and 38 per cent. in the two mixtures of ethyl alcohol and water and to 35 per cent. in the mixture of propyl alcohol and water. The proportion of  $\alpha$ -galactose when equilibrium is attained is therefore reduced in the same ratio from one-half almost to one-third of the total weight of sugar in solution on passing from the anhydrous to the aqueous-alcoholic solutions. The significance of this result, which finds a parallel in the case of glucose, is discussed in a subsequent section.

FIG. 3.

TABLE II.—*Solubility of Galactose in Aqueous Alcohol at 20°.*

I. $C_2H_6O + H_2O$ .			II. $C_2H_6O + 2H_2O$ .			III. $C_3H_8O + 2H_2O$ .		
Time.	$\alpha_D$ . Initial.	$\alpha_D$ . Final.	Time.	$\alpha_D$ . Initial.	$\alpha_D$ . Final.	Time.	$\alpha_D$ . Initial.	$\alpha_D$ . Final.
0 h.	—	[55']	0 h.	—	[2°24']	0 h.	—	[1°55']
0.6 h.	1°39'	1° 4'	0.6 h.	4° 5'	2 45	0.6 h.	3°33'	2 16
3.1 h.	1 56	1 31	1.1 h.	4 18	2 53	3.5 h.	4 19	3 35
9.4 h.	2 13	2 6	2.1 h.	—	3 29	7.0 h.	4 37	4 39
25 h.	2 19	2 22	3.3 h.	4 42	3 52	9.5 h.	5 16	5 2
31.2 h.	2 24	2 24	4.2 h.	—	4 8	Final	—	5 25
3 days	—	2 20	5.3 h.	—	4 32			
			7.6 h.	5 20	5 2			
			9.5 h.	5 29	5 17			
			11.6 h.	—	5 35			
			Final	—	6 16			

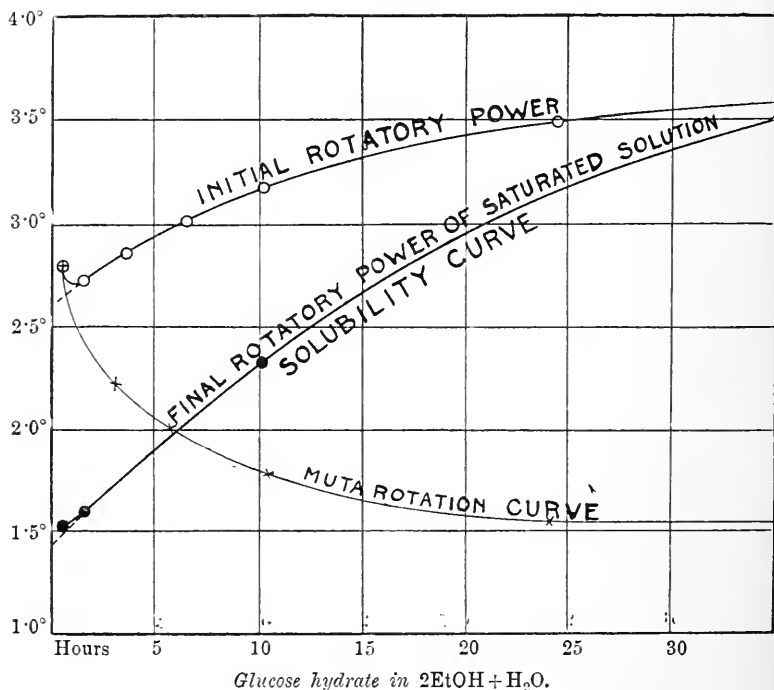
Ratio 55'/2°22' = 39%	Ratio 2°24'/6°16' = 38%	Ratio 1°55'/5°25 = 35%
Water in solvent = 28%	Water in solvent = 44%	Water in solvent = 37%
Half-period, 3.5 hours.	Half-period, 1.3 hours.	Half-period, 2.25 hours.

*Solubility of Glucose in Aqueous Alcohol. Formation of a Hydrate.*

When  $\alpha$ -glucose is brought into contact with aqueous alcohol, it is converted into a hydrate having the composition  $C_6H_{12}O_6 \cdot H_2O$ . This hydrate, which is much less soluble than  $\alpha$ -glucose, is formed in the case of alcohol containing 28 or 16 per cent. of water; the minimum proportion of water required for its formation has not been determined.

When the hydrate (separated from a previous experiment) was used

FIG. 4.

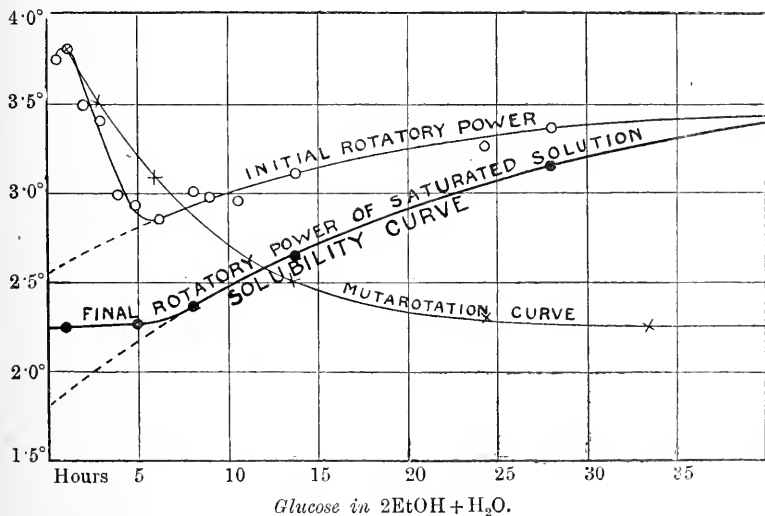


as the solid phase in a series of solubility measurements, its behaviour was quite normal. Thus, the measurements with a mixture of the composition  $(2C_2H_6O + H_2O)$ , which are recorded in Table III and represented graphically in Fig. 4, are strictly comparable with the measurements of anhydrous  $\alpha$ -galactose which have already been described. So also the dotted curve for glucose hydrate in contact with a mixture of the composition  $(C_2H_6O + H_2O)$ , shown in Fig. 6 (p. 1562), is normal in character and does not differ from the typical form of

the curves for the anhydrous sugars. The ratio of the initial to the final solubility of glucose hydrate in the mixture ( $\text{EtOH} + 2\text{H}_2\text{O}$ ) is 0.45; in the mixture ( $\text{EtOH} + \text{H}_2\text{O}$ ) it is 0.40, the latter value corresponding closely with the figure 0.39 for anhydrous galactose in the same solvent.

A very different series of changes is observed when anhydrous  $\alpha$ -glucose is brought into contact with a mixture of alcohol and water which is sufficiently dilute to convert the solid glucose into its hydrate. Initially, the solution becomes saturated with anhydrous glucose; it is then supersaturated with regard to the hydrate and the latter soon crystallises from the solution, replacing the anhydrous sugar as the solid phase or equilibrator in the system. This crystallisation is

FIG. 5.

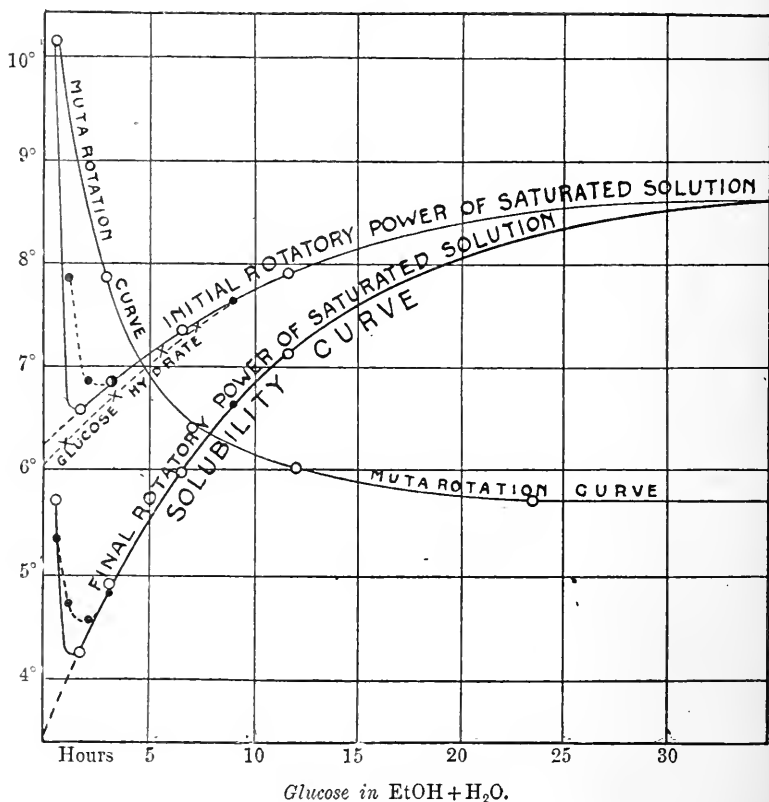


clearly visible to the eye; the sugar, which was initially in the form of a very fine powder floating freely in the solution, becomes caked as the hydrate separates and the sides of the bottle become covered with glistening crystals. The hydrate is deposited in so coarse a form that the sugar no longer remains suspended in the solution; in order to ensure a constant saturation, it is desirable to remove the solution from the thermostat and rapidly powder the separated crystals.

The effect of these changes is very clearly shown by observations of the initial and final rotatory powers of the samples of the saturated solution drawn off from time to time. The curves for  $\alpha$ -glucose in contact with the mixture ( $\text{EtOH} + \text{H}_2\text{O}$ ), which are shown in Fig. 6, afford especially clear evidence of the initial super-

saturation of the solution, being characterised by a rapid initial decrease of rotatory power, which precedes the normal increase due to isomeric change. This decrease is shown in a very striking way by the curves of initial rotatory power, which in one series of observations fell abruptly from  $10.2^\circ$  to  $6.5^\circ$  during the interval between 0.5 and 1.6 hours, whilst in a duplicate experiment (shown in Fig. 6 by black dots joined by a broken line) a less marked fall from  $7.9^\circ$  to  $6.9^\circ$

FIG. 6.



was noticed during the second hour of the experiment. It may be noted that, in the latter case, two earlier observations at about 0.5 and 0.6 hour had to be abandoned on account of the separation in the filtering tube of a large quantity of crystals of the hydrate. That there is actually a decrease in the weight of sugar in solution is shown by the fall in the curve of final rotatory powers, since these values are approximately proportional to the concentration of the solution.

The behaviour of  $\alpha$ -glucose in contact with a mixture having approximately the composition ( $2\text{EtOH} + \text{H}_2\text{O}$ ) is in most respects similar to that just described; one important difference was noticed, however, between the two series of observations. In the preceding series, in which more dilute alcohol was used, the separation of the hydrate was rapid, and although it was remarkable that it should be necessary to stir during one to two hours in order to remove the excess of sugar from the solution, it was thought that the phenomenon was merely one of supersaturation. From the less dilute alcohol, the separation of the hydrate took place so slowly that it was exactly balanced by the increased solubility due to isomeric change, the weight of sugar in solution remaining substantially constant during the first 5 hours. This constant solubility is shown by the horizontal line at the commencement of the solubility curve in Fig. 5; it was observed in three independent series of experiments. After about 5 hours, the solubility increased in the normal way, reaching a limiting value at the end of three days.

As the weight of sugar in solution was substantially constant during the first five hours, the conditions were essentially those of a simple mutarotation experiment in which no solid sugar is present. This similarity of conditions is shown by the nearly parallel courses of the curves which represent (1) the mutarotation of one of the early samples and (2) the initial rotatory powers of the freshly filtered samples withdrawn from time to time.

These observations show that the conversion of  $\alpha$ -glucose into its hydrate by means of aqueous alcohol is not an instantaneous process, as the separation of the hydrate from alcohol containing 16 per cent. of water is not complete until after 5 hours; even in contact with alcohol containing 28 per cent. of water, the change occupies from one to two hours. In aqueous solutions, the hydration of the sugar appears to be almost instantaneous, since it is not possible to detect a difference between the behaviour of solutions prepared from anhydrous and from hydrated glucose. Thus a 5 per cent. solution of the hydrate in water gave  $[\alpha]_D + 102^\circ$  at 8 minutes, decreasing to  $97^\circ$  in 15 minutes and ultimately to  $48.4^\circ$ . When reckoned on anhydrous glucose, this gives  $[\alpha]_D + 112^\circ$ , decreasing to  $107^\circ$  and  $53^\circ$ , values which closely resemble those for the anhydrous sugar. The initial rotatory power is somewhat higher than that usually observed with  $\alpha$ -glucose but the difference is not large; it is probably due to secondary causes such as the exceptional freedom of the hydrate from  $\beta$ -glucose and the slightly different conditions attending the dissolution.

The dissolution of powdered glucose in water takes place very rapidly if the mixture is shaken immediately after adding the water.

But if the sugar is allowed to remain still a few seconds, the solid forms a cake which dissolves only slowly. This behaviour is closely analogous with that of the sugar when stirred with aqueous alcohol and indicates the occurrence of a similar process of hydration in the initial stages of the interaction.

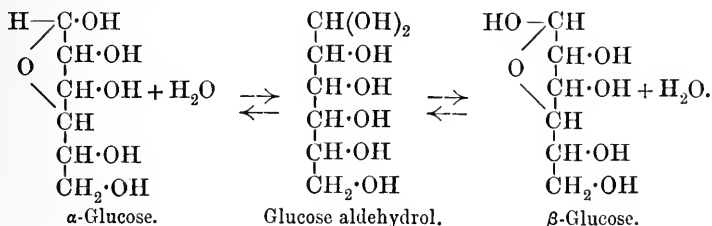
TABLE III.—*Solubility of Glucose in Aqueous Alcohol.*

I. Glucose hydrate in EtOH + H <sub>2</sub> O (Fig. 6).			II. Anhydrous glucose in EtOH + H <sub>2</sub> O (Fig. 6).			III. Anhydrous glucose in EtOH + H <sub>2</sub> O (Fig. 6).		
Time.	$\alpha_D$ . Initial.	$\alpha_D$ . Final.	Time.	$\alpha_D$ . Initial.	$\alpha_D$ . Final.	Time.	$\alpha_D$ . Initial.	$\alpha_D$ . Final.
0 h.	[6° 4']	—	0.5 h.	10° 11'	5° 42'	0.5 h.	—	5° 20'
1 h.	6 16	3° 37'	1.6 h.	6 34	4 15	1.1 h.	7° 52'	4 43
3 h.	6 37	—	3.2 h.	6 52	4 54	2.1 h.	6 52	4 35
5.5 h.	7 8	—	6.5 h.	7 21	5 59	3.2 h.	6 51	4 49
7 h.	7 22	—	11.7 h.	7 54	7 7	9 h.	7 41	6 37
10 h.	7 52	—	23.4 h.	8 16	8 13	29.6 h.	8 10	7 47
1 day	—	8 37	30.3 h.	—	8 40	55.3 h.	8 34	—
			47.4 h.	—	8 37			
			6 days	—	8 41			
			Final	—	8 35			
						8° 38'		

## THEORETICAL CONSIDERATIONS.

 1. *The Mechanism of Isomeric Change.*

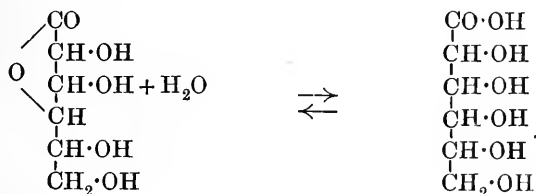
In order to explain the interconversion of  $\alpha$ - and  $\beta$ -glucoses, it was suggested in a recent paper (Trans., 1903, 83, 1314) that the mixture of sugars which is formed on dissolving glucose in water contains, in addition to the stereoisomeric oxides, the aldehydic form of the sugar or its hydrate. It was further suggested that this substance is a necessary intermediate product in the conversion of  $\alpha$ - into  $\beta$ -glucose and *vice versa*. In aqueous solutions, the aldehyde would probably be completely hydrated. The equilibrium was therefore represented by the scheme:



This scheme is intermediate in character between that of Emil Fischer—which represented the mutarotation of glucose in aqueous solution as being wholly due to the hydration of the sugar—and the more recent view that the mutarotation is wholly due to isomeric change.

The enolic form of the sugar is probably also present in the solutions; the slow rate at which glucose, mannose and fructose are converted into one another, even in presence of large quantities of catalyst, indicates, however, that the proportion of enol must be exceedingly small.

The view that the interconversion of  $\alpha$ - and  $\beta$ -glucoses depends on the splitting of the oxide ring receives very strong support from the fact that gluconic lactone and a number of similar compounds have been shown to undergo reversible hydrolysis and to exhibit mutarotation when dissolved in water:



Although  $\alpha$ - and  $\beta$ -glucoses are not technically included amongst the lactones, they differ from gluconic lactone only in the presence of  $>\text{CO}$  in place of  $>\text{CH}\cdot\text{OH}$ ; they may therefore be expected to show many of the properties of the lactone, including the partial hydrolysis which it undergoes in aqueous solutions.

Although no direct evidence has been obtained as to the nature of the intermediate products, the observations recorded above are all in accordance with the theory that isomeric change is dependent on the hydrolysis of the oxide ring. In anhydrous methyl alcohol, in which the formation of hydrate can only take place to a very small extent, isomeric change is exceedingly slow. As water is added to the alcohol, the velocity of change increases, reaching a maximum value in aqueous solutions. This increase of velocity is exactly what might be expected to follow from an increase in the proportion of the intermediate hydrate (aldehydrol) in the aqueous-alcoholic solution.

The presence of an increasing quantity of the aldehydrol would also account for the decreasing proportion of  $\alpha$ -sugar in the more aqueous solutions, a subject that is more fully discussed below.

In their recent investigation of the tetramethyl glucoses, Purdie and Irvine (Trans., 1904, 85, 1049—1070) have been able to extend their observations to solvents such as carbon tetrachloride and benzene, in which glucose itself is altogether insoluble. These observations have an important bearing on the explanation of the manner in which isomeric change takes place in this series of compounds, since it would appear at first sight that the theory of hydrocatalysis is hardly applicable to this case. The rate of change is, however, even less than in methyl alcohol, and H. E. Armstrong has pointed out that, although the proportion of water in these solvents may be small, the whole of it is available for hydrolysis, whereas in methyl alcohol the activity of the water is greatly lessened by combination with the alcohol. It is therefore by no means improbable that in this case also isomeric change is conditioned by the presence of water and involves the formation of small quantities of an intermediate hydrated sugar such as the above-mentioned aldehydrol.

## 2. *The Nature of Glucose Hydrate.*

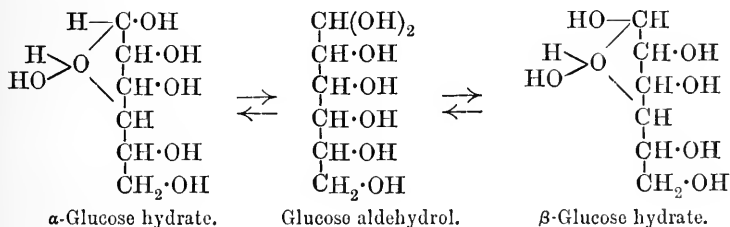
In considering the nature of glucose hydrate, it is necessary to take into account three principal facts.

(1) Glucose, whether anhydrous or hydrated, gives solutions of similar rotatory power when freshly dissolved in water, the conversion of the anhydrous sugar into the hydrate appearing to take place almost instantaneously. This observation indicates that the hydrate is closely related to  $\alpha$ -glucose and cannot be the aldehydrol formu-

lated above as an intermediate product in the interconversion of  $\alpha$ - and  $\beta$ -glucoses.

(2) This conclusion is supported by the fact that the increment of solubility of glucose hydrate in aqueous alcohol is similar to that of anhydrous  $\alpha$ -galactose in the same solvent; the hydrate, in fact, behaves as if it were merely a compound of anhydrous  $\alpha$ -glucose with one molecular proportion of water of crystallisation.

(3) This simple view requires development in consideration of the fact that the conversion of the anhydrous sugar into the hydrate by aqueous alcohol requires a period of from one to five hours. The persistent supersaturation of the solutions when in contact with crystals of the solid hydrate is not in accord with the usual behaviour of compounds containing water of crystallisation; it is probable that the hydrate, although rapidly formed from  $\alpha$ -glucose, is not merely a molecular compound but possesses a distinct structural formula, such, for instance, as that of the oxonium hydroxide,  $\text{>O} \begin{smallmatrix} \text{H} \\ \diagup \\ \text{O} \end{smallmatrix} \text{H}$  (E. F. Armstrong, Trans., 1903, 83, 1309). If this compound were rapidly formed in the solution, it would probably be indistinguishable from  $\alpha$ -glucose and the velocity of isomeric change would be determined almost entirely by the much slower rate at which the oxonium hydroxide was converted into the aldehydrol and *vice versa*. The essential part of the change in aqueous solution would then be represented by the scheme:



### 3. Results of the Solubility Measurements. The possible presence of a Third Form of the Sugar in the Aqueous-alcoholic Solutions.

The experiments described above indicate that in methyl-alcoholic solutions of glucose and galactose one-half of the sugar is in the  $\alpha$ -form, whilst in aqueous alcohol the proportion appears to be considerably less. This is shown in the following table:

TABLE IV.

Sugar.	Solvent.	Percentage of water in solvent.	Percentage proportion of $\alpha$ -sugar.	Half-period.
Glucose .....	MeOH	—	52	36 hours
Galactose .....		—	50	—
Glucose .....	2EtOH + H <sub>2</sub> O	16	45	12.5 hours
" .....	EtOH + H <sub>2</sub> O	28	40	7.5 "
Galactose .....		28	39	3.5 "
" .....	EtOH + 2H <sub>2</sub> O	44	38	1.3 "
" .....	PrOH + 2H <sub>2</sub> O	37	35	2.25 "

Two explanations may be given of the decreasing proportion of  $\alpha$ -sugar in the aqueous-alcoholic solutions.

(1) It may be supposed that the increase of solubility is due entirely to isomeric change but that the proportions of  $\alpha$ - and  $\beta$ -glucoses differ considerably in different solvents.

(2) It may be supposed that the relative proportions of  $\alpha$ - and  $\beta$ -glucoses remain unaltered but that other substances, such as the aldehydic form of the sugar or its hydrate, are present in the aqueous solutions.

Of these explanations, the latter is for the following reasons by far the more probable.

(1) The former assumption implies that in the aqueous-alcoholic solutions the  $\beta$ -sugar is the stable form, although the  $\alpha$ -sugar is the first to separate from the solution. This is not impossible, since cases are known in which the minor constituent separates first; but at least in the case of glucose it implies a reversal of stability on changing the solvent, since in the methyl-alcoholic solutions the  $\alpha$ -form is slightly predominant.

(2) Although in certain instances there is a marked alteration in the proportions in which dynamic isomerides are in equilibrium, when the temperature, solvent, or concentration is changed, these variations are usually associated with some marked difference in type between the isomerides. Thus, if one isomeride has a tendency to polymerise, the proportion of this form may be reduced by using a dissociating solvent or by raising the temperature. And if one of the isomerides is an electrolyte, whilst the other is a dielectric, an ionising solvent will favour the formation of the former. But in the case of the stereoisomeric  $\alpha$ - and  $\beta$ -glucoses, the two compounds are of precisely similar type, and differ only in the configuration of one of the five asymmetric carbon atoms. It is therefore unlikely that the solvent

would have any marked selective action on the two isomerides or favour the formation of one compound at the expense of the other. Such a selective effect is the less likely in view of the fact that (1) in methyl-alcoholic solutions there is no marked difference between the stability of the  $\alpha$ - and  $\beta$ -sugars; and (2) that glucose and galactose behave in the same way both in anhydrous and in aqueous alcohol, although they differ in structure to an extent that is at least as marked as in the case of  $\alpha$ - and  $\beta$ -glucoses or  $\alpha$ - and  $\beta$ -galactoses.

(3) The view that the decreasing proportion of  $\alpha$ -sugar in the aqueous-alcoholic solutions is due to the presence of a third form of the sugar, rather than to an alteration in the relative stability of the  $\alpha$ - and  $\beta$ -forms, involves no novel assumption but, on the contrary, is entirely in accord with conclusions previously arrived at from a consideration of the probable mechanism of isomeric change (*loc. cit.*, p. 1316). At the present time, indeed, it is generally recognised that  $\alpha$ - and  $\beta$ -glucoses are not converted into one another by a direct interchange of the radicles of the terminal  $\text{>C<}^{\text{H}}_{\text{OH}}$  group, but that isomeric change proceeds by means of a mechanism which involves the formation of one or more intermediate substances. The only question that remains open to dispute is with regard to the nature of the intermediate product and the proportions in which it is present in the solution. The reasons for thinking that the chief intermediate product is the aldehydic form of the sugar or its hydrate have already been discussed and need not again be stated, as the exact nature of this substance is only of secondary importance in connection with the problem now under discussion.

(4) Attention may, however, be called to the evidence afforded by the data given in the last column of Table IV, which show the periods required for the solubility to reach a mean between its initial and final values. These figures show that on passing from the anhydrous to the aqueous alcoholic solutions there is a great increase in the velocity with which equilibrium is attained and therefore indicate that the proportion of intermediate substance is many times greater in the aqueous than in the anhydrous solutions. This conclusion is identical with that arrived at from a consideration of the increments of solubility of  $\alpha$ -glucose and  $\alpha$ -galactose in these solvents and lends additional support to the view that the aqueous solutions contain a considerable proportion of a third form of the sugar. In the anhydrous methyl-alcoholic solutions, on the other hand, the velocity of change is so slow that the proportion of intermediate substance in the solution must be very small, the solute probably consisting almost wholly of the  $\alpha$ - and  $\beta$ -oxidic forms of the sugar.

*Summary and Conclusions.*

The main result of the experiments now described is to show that in the case of glucose and galactose the proportion of  $\alpha$ -sugar in solution decreases as the amount of water in the solvent increases. This result is ascribed to the presence in the aqueous solutions of a third form of the sugar.

In methyl-alcoholic solutions, one-half of the sugar is in the  $\alpha$ -form. The remainder probably consists almost entirely of the  $\beta$ -sugar, since the third form can be present only in very minute quantities. The  $\alpha$ - and  $\beta$ -forms are therefore equally stable in the solution, although the  $\alpha$ -form, being the less soluble, is the first to crystallise when the solution is evaporated.

In the mixture ( $\text{EtOH} + \text{H}_2\text{O}$ ), the proportion of  $\alpha$ -sugar falls to 40 per cent. This might be due to the presence of 60 per cent. of the  $\beta$ -sugar. A more probable explanation is that the solution contains equal proportions of the  $\alpha$ - and  $\beta$ -forms, namely, 40 per cent. of each, 20 per cent. of the sugar being present in a third hydrated form.

On account of the excessive solubility of glucose and galactose in water, the measurements could not be extended to aqueous solutions but it is clear that an even smaller ratio of initial to final solubility must be anticipated under these conditions. It is, therefore, evident that although in anhydrous solvents the mutarotation of glucose and galactose may be almost wholly due to isomeric change, the change of rotatory power in aqueous solutions may be to a large extent due to the formation of a third hydrated form of the sugar.

It is considered probable that the third form of the sugar is the aldehydrol and that this forms an intermediate stage in the inter-conversion of the stereoisomeric  $\alpha$ - and  $\beta$ -sugars.

The author is indebted to Professor Armstrong for much help in the preparation of the present paper, and desires to take this opportunity of expressing his thanks.

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CLVIII.—*Position-Isomerism and Optical Activity. The Methyl and Ethyl Esters of Di-o-, -m-, and -p-nitrobenzoyltartaric Acids.*

By PERCY FARADAY FRANKLAND and JOHN HARGER, Ph.D.

THE only recorded observations concerning the rotatory influence of the three isomeric nitrobenzoyl groups are due to Goldschmidt and Freund (*Zeit. physikal. Chem.*, 1894, 14, 394), who introduced these substituents into ordinary *d*-carvoxime, and obtained the following specific rotations of the isomeric products in chloroform solution :

Nitrobenzoyl- <i>d</i> -carvoximes.	$[\alpha]_D$ .	Concentration.
Ortho-compound .....	0°	4·7044
Ortho-        „        .....	0	4·5575
Meta-        „        .....	+ 20·68	4·5845
Para-        „        .....	+ 17·33	4·5648

The above derivatives were prepared from a carvoxime having  $[\alpha]_D + 39·62^\circ$  (in absolute alcoholic solution,  $c = 9·8398$ ). The inactivity of the ortho-compound is remarkable, as it cannot be explained by racemisation, since, on hydrolysis with sodium hydroxide, a dextro-rotatory and not an inactive carvoxime was obtained. From analogy with other position-isomeric active compounds, it would be anticipated that, in this case, the ortho-compound should have the highest dextro-rotation of the three.

In order to investigate further the rotatory influence of the three isomeric nitrobenzoyl groups, we have introduced them into dimethyl and diethyl tartrates, and have prepared the three isomeric dimethyl and the three diethyl dinitrobenzoyltartrates, determining their rotations in the liquid state over a wide range of temperature.

Dimethyl tartrate has  $[\alpha]_D^{20^\circ} + 2·14^\circ$  and diethyl tartrate  $[\alpha]_D^{20^\circ} + 7·67^\circ$  whereas all these dinitrobenzoyltartrates have a high lævorotation, the rotation of the methyl being greater than that of the ethyl compounds, and, again, whilst the para-isomeride has in each case a higher rotation than the meta-compound, the relative rotatory value of the *o*-nitrobenzoyl group is entirely dependent on temperature. Thus, in the case of the ethyl derivatives, at  $15^\circ$  the ortho compound has the highest rotation, whilst at  $180^\circ$  it has the lowest rotation of the three; on the other hand, over the whole of this range of temperature the rotation of the para-isomeride is markedly greater than that of the meta-compound. The same relations doubtless hold good in the case of the methyl derivatives, but for the ortho-compound we have only determined the rotation at  $100^\circ$  and  $109^\circ$ .



		M. p.
<i>o</i> -Chlorobenzenesulphonamide .....		188°
<i>p</i> - " .....		143
<i>o</i> -Bromobenzenesulphonamide .....		186
<i>p</i> - " (Nölting) .....		166
	(Goslich) .....	160—161
<i>o</i> -Nitromandelic acid .....		140
<i>p</i> - " " .....		126
<i>o</i> -Bromobenzyl alcohol .....		80
<i>p</i> - " " (Jackson, Lowery, <i>Amer. Chem.</i>		
	<i>J.</i> , 1881, 3, 246) .....	77
	(Errera, <i>Gazzetta</i> , 1888, 18, 238).	75

It is noteworthy that all the foregoing pairs of isomerides excepting one contain nitrogen.

As regards molecular volume, we can only institute a complete comparison in the case of the ethyl compounds, as we were not able to obtain density determinations for the ortho-methyl derivative. In the case of the three isomeric ethyl compounds, the molecular volumes follow in the same order as the rotations, that of the para- being the greatest and that of the ortho-compound the least.

		Molecular volume at 15°.	
		Calculated.	Found.
Diethyl di- <i>p</i> -nitrobenzoyltartrate.....	366·7	$\frac{504}{1.3362}$	= 377·2
" di- <i>m</i> - "	"	$\frac{504}{1.3581}$	= 371·1
" di- <i>o</i> - "	"	$\frac{504}{1.3720}$	= 367·3*

In the case of the methyl compounds also the para- has a greater molecular volume than the meta-derivative at the temperatures at which their rotations were determined.

A similar relationship between the magnitudes of the rotations and molecular volumes has been found by one of us to hold good in the following cases of the three isomeric ethyl monitoluyltartrates (P. Frankland and McCrae, *Trans.*, 1898, 73, 324), the ethyl ditoluyltartrates (P. Frankland and Wharton, *Trans.*, 1896, 69, 1309), the methyl ditoluylglycerates, and the ethyl ditoluylglycerates (P. Frankland

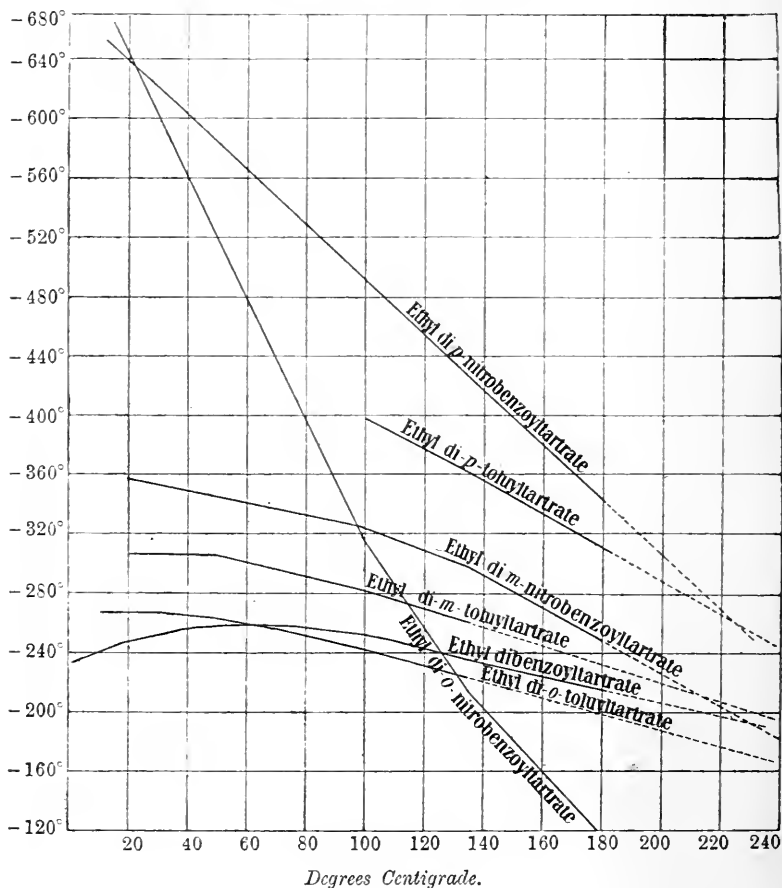
\* It should be pointed out that all the density determinations of the ortho-compound were made at temperatures above that at which its rotation falls below that of the meta-isomeride.

The constants used in the calculation of the molecular volume were: C=9·9, H=3·1, O=5·5, N in NO<sub>2</sub>=10·7, covolume=+25·9, benzene ring= -13·2 (Traube, *Ber.*, 1895, 28, 2724, 2924).

and H. Aston, Trans., 1899, 75, 499), whilst the same relationship is almost preserved in the case of the methyl ditoluyltartrates, in which, however, the meta- has a very slightly greater molecular volume than the para-compound, although the rotation of the latter exceeds that of

DIAGRAM I.

[M]<sub>D</sub> *Ethyl dinitrobenzoyltartrates.*  
*Ethyl ditoluyltartrates.*



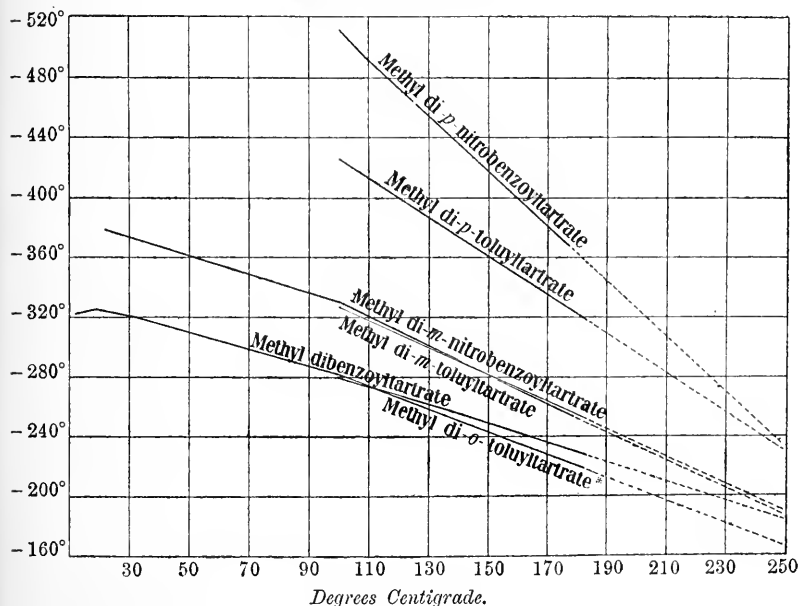
the former. Again, the methyl and ethyl toluylmalates (P. Frankland and Wharton, Trans., 1899, 75, 337) exhibit the same relationship between the rotatory effect and the molecular volume.

The molecular rotations of the nitrobenzoyl- and toluyltartrates enable a comparison to be instituted between the rotatory effects of

the nitro- and the methyl groups respectively when acting as substituents in the benzene ring. From the accompanying diagrams it will be seen that, whether we consider the methyl or the ethyl derivatives, the nitrobenzoyl has a higher rotation than the corresponding toluyl compound, excepting in the case of the ethyl *o*-nitro-derivative, of which at lower temperatures the rotation is, as already mentioned, enormously greater than at higher temperatures, and at the latter it

DIAGRAM II.

[M]<sub>D</sub> *Methyl dinitrobenzoyltartrates.*  
*Methyl ditoluyltartrates.*



\* This name refers to the longer curve.

will be seen that its rotatory effect falls below that of the corresponding *o*-toluyl compound.

It has, however, already been shown by one of us (P. Frankland and Wharton, *Trans.*, 1896, 69, 1583) that the rotatory effect of the benzoyl group is diminished by substituting an atom of hydrogen in the ortho-position by methyl, so that if the rotatory value of the nitro-group is greater than that of methyl, the *o*-nitrobenzoyl should have a smaller rotatory effect than the *o*-toluyl group, and the normal part of the molecular rotation curve for ethyl di-*o*-nitrobenzoyltartrate would be that portion which falls below the curve for ethyl di-*o*-toluyltartrate, and the other part of the curve, which lies entirely below

the melting point of the *o*-nitrobenzoyl compound, should be regarded as abnormal.

Again, it should be pointed out that the rotations of the nitrobenzoyl compounds diminish more rapidly with increase of temperature than do those of the toluyll compounds, so that at very high temperatures, somewhat beyond those to which our observations were carried, the molecular rotations of even the *m*- and the *p*-nitrobenzoyl derivatives fall below those of the corresponding toluyll compounds, which is indicated in the diagrams by the intersection of the dotted lines. Both in the case of the methyl and ethyl derivatives, this intersection takes place at a lower temperature for the meta- than for the para-compounds.

#### EXPERIMENTAL.

*p*-Nitrobenzoyl Chloride.—Fifty grams of *p*-nitrobenzoic acid (m. p. 238°) were mixed with 64 grams of phosphorus pentachloride, and when the visible reaction had ceased, the mixture was heated for half an hour on the water-bath and then fractionated under reduced pressure. The yield was 98 per cent. of the theoretical, the boiling point being 150—152° (15 mm.). The product was redistilled several times until free from phosphorus, and, owing to the difficulty of getting rid of the latter, it was found preferable to use the theoretical amount of phosphorus pentachloride instead of the excess employed above.

The *p*-nitrobenzoyl chloride solidified as a yellow, crystalline mass which, when recrystallised from light petroleum, melted at 75°.

*m*-Nitrobenzoyl Chloride.—*m*-Nitrobenzoic acid (150 grams), purified by crystallisation from methylated spirit and melting at 140°, was treated as above with 187 grams of phosphorus pentachloride; 146 grams of phosphorus-free product were obtained, the yield being 88 per cent. of the theoretical (Richardson, *Ber.*, 1879, 12, 351; Claisen and Thompson, *ibid.*, 1943).

*o*-Nitrobenzoyl Chloride.—*o*-Nitrobenzoic acid (100 grams) was treated as before with 123 grams of phosphorus pentachloride, and 98 grams of pure product were obtained, being equivalent to a yield of 88 per cent. (Claisen and Shadwell, *Ber.*, 1879, 12, 350).

Diethyl Di-*p*-nitrobenzoyltartrate.—Seventeen grams of diethyl tartarate were added in small quantities to 43 grams of *p*-nitrobenzoyl chloride at 140°, the temperature being finally raised to 200—220° for 3 hours in order to complete the reaction. The excess of acid chloride was distilled off under reduced pressure, and the sticky residue was dissolved in ether and shaken for 5 hours with aqueous sodium carbonate, this treatment being repeated several times with fresh quantities of sodium carbonate solution. The ethereal solution was evaporated, the residue dried in the steam oven and then crystallised from methylated spirit.

The substance separates from the alcohol on cooling, in long needles, melting at 124—124·5°: the yield of crude product was 88 per cent. of the theoretical.

0·4153 gave 20·2 c.c. moist nitrogen at 9° and 748·7 mm.  $N = 5·76$ .  
 0·3014 „ 14·05 c.c. „ „ at 10° and 757·8 mm.  $N = 5·56$ .  
 $C_{22}H_{20}O_{12}N_2$  requires  $N = 5·56$  per cent.

The following density determinations were made of the substance in the liquid state :

$d_{95^\circ/4^\circ} = 1·2682$ ,  $d_{120^\circ/4^\circ} = 1·2470$ ,  $d_{141^\circ/4^\circ} = 1·2273$   
 $M.V._{95^\circ} = 397·4$ ,  $M.V._{120^\circ} = 404·2$ ,  $M.V._{141^\circ} = 410·7$ .

*Rotation of Diethyl Di-p-nitrobenzoyltartrate.*

Temp.	$\alpha_D$ for $l=1$ .	$d_{t^\circ/4^\circ}$ .	$[\alpha]_D$ .	$[M]_D$ .
13°	-173°	1·3377	-129·33°	-651·8°
99	123·4	1·2648	97·57	491·8
135	105·37	1·2329	85·47	430·8
138	102·6	1·2301	83·41	420·4
181	80·7	1·1898	67·83	341·9

*Dimethyl Di-p-nitrobenzoyltartrate.*

The method of preparation was exactly similar to that employed for the ethyl compound, excepting that the residue after distilling off the excess of acid chloride became solid on stirring, and was then washed with aqueous sodium carbonate; the theoretical yield being thus obtained. The substance was purified by dissolving in chloroform, to which was added methylated spirit, when the compound slowly separated in very short needles melting at 140°; it is very soluble in chloroform or benzene, sparingly soluble in cold and moderately so in hot methylated spirit, it dissolves readily in ether, and with difficulty in light petroleum.

0·3290 gave 17·6 c.c. moist nitrogen at 13° and 757·9 mm.  $N = 6·30$ .  
 0·3425 „ 18·17 c.c. „ „ at 15° and 737·4 mm.  $N = 6·02$ .  
 $C_{20}H_{16}O_{12}N_2$  requires  $N = 5·88$  per cent.

The following density determinations were made of the substance in the liquid state :

$d_{113^\circ/4^\circ} = 1·3142$ ,  $d_{116·5^\circ/4^\circ} = 1·3104$ ,  $d_{138^\circ/4^\circ} = 1·2905$ .  
 $M.V._{113^\circ} = 362·2$ ,  $M.V._{116·5} = 363·2$ ,  $M.V._{138} = 368·8$ .

*Rotation of Dimethyl Di-p-nitrobenzoyltartrate.*

Temp.	$\alpha_D$ for $l=1$ .	$d\ell/4^\circ$ .	$[\alpha]_D$	$[M]_D$ .
100°	-142.62°	1.3260	-107.56°	-512.0°
108.3	137.2	1.3183	104.07	495.4
136	120.13	1.2923	92.96	442.5
178	96.63	1.2531	77.11	367.0

*Diethyl Di-m-nitrobenzoyltartrate.*

The only modifications introduced into the general method of preparation already described were that the mixture of diethyl tartrate and acid chloride was only heated to 180° for 4 hours, and that the residue, after distilling off excess of acid chloride, was shaken in chloroform solution with aqueous sodium carbonate. The substance was obtained solid by mixing with ether, and stirring well during the evaporation of the latter; it was left on a porous plate until quite hard, and then repeatedly crystallised from hot methylated spirit until the melting point was constant. The substance forms long, yellowish-white needles melting at 95.8° to a yellow liquid.

0.4687 gave 25.2 c.c. moist nitrogen at 20.5° and 743.2 mm.  $N=5.99$ .

$C_{22}H_{20}O_{12}N_2$  requires  $N=5.56$  per cent.

The following density determinations were made on the liquid substance:

$d_{35}^{40} = 1.3351$ ,  $d_{84}^{40} = 1.2788$ ,  $d_{127}^{40} = 1.2419$ .

$M.V._{35} = 377.5$ ,  $M.V._{84} = 394.1$ ,  $M.V._{127} = 405.8$ .

*Rotation of Diethyl Di-m-nitrobenzoyltartrate.*

Temp.	$\alpha_D$ for $l=1$ .	$d\ell/4^\circ$ .	$[\alpha]_D$ .	$[M]_D$ .
20°	-95.36°	1.3449	-70.90°	-357.3°
100	81.59	1.2679	64.35	324.3
135	73.08	1.2342	59.21	298.4
181	58.41	1.1900	49.08	247.4

*Dimethyl Di-m-nitrobenzoyltartrate.*

This was prepared in the usual manner by the interaction of the acid chloride and dimethyl tartrate, the highest temperature used being 180°. After distilling off the excess of acid chloride, the residue was dissolved in chloroform and washed with a solution of sodium carbonate; the sticky mass left after distilling off the chloroform was treated with ether, which removed a quantity of liquid matter; the solid residue was repeatedly crystallised from methylated spirit and finally melted at 117.8°.

0.4815 gave 25.8 c.c. moist nitrogen at 20.5° and 743.2 mm.  $N = 5.97$ .

$C_{20}H_{16}O_{12}N_2$  requires  $N = 5.88$  per cent.

$d_{92^\circ/4^\circ} = 1.3512$ ,  $d_{103^\circ/4^\circ} = 1.3473$ ,  $d_{130^\circ/4^\circ} = 1.3389$ .

$M.V._{92^\circ} = 352.3$ ,  $M.V._{103^\circ} = 353.3$ ,  $M.V._{130^\circ} = 355.5$ .

*Rotation of Dimethyl Di-m-nitrobenzoyltartrate.*

Temp.	$\alpha_D$ for $l=1$ .	$d_{t^\circ/4^\circ}$ .	$[\alpha]_D$ .	$[M]_D$ .
22°	-109.20°	1.3760	-79.36°	-377.8°
100	93.33	1.3484	69.22	329.5
109	90.24	1.3454	67.07	319.3
137	82.71	1.3367	61.88	294.5
179.5	70.64	1.3236	53.37	254.0

*Diethyl Di-o-nitrobenzoyltartrate.*

In the interaction of the acid chloride (30 grams) with diethyl tartrate (12 grams) the temperature was not allowed to rise above 160°. Instead of distilling off the excess of acid chloride, it was washed out by means of sodium carbonate solution, the substance being dissolved in chloroform. On distilling off the chloroform, a dark red, crystalline mass was left, which was almost insoluble in methylated spirit, but easily soluble in chloroform; this was readily purified by dissolving in hot chloroform and adding hot methylated spirit, when the mixture, on cooling, deposited long, white needles, whilst the red colouring matter remained in solution. The melting point was 143°.

0.4459 gave 22.9 c.c. moist nitrogen at 21° and 758 mm.  $N = 5.83$ .

$C_{22}H_{20}O_{12}N_2$  requires  $N = 5.56$  per cent.

The following density determinations were made on the liquid substance:

$d_{105^\circ/4^\circ} = 1.2739$ ,  $d_{139^\circ/4^\circ} = 1.2368$ ,  $d_{152.5^\circ/4^\circ} = 1.2233$ .

$M.V._{105^\circ} = 395.6$ ,  $M.V._{139^\circ} = 407.5$ ,  $M.V._{152.5^\circ} = 412.0$ .

*Rotation of Diethyl Di-o-nitrobenzoyltartrate.*

Temp.	$\alpha_D$ for $l=1$ .	$d_{t^\circ/4^\circ}$ .	$[\alpha]_D$ .	$[M]_D$ .
15°	-180.90°	1.3720	-131.85°	-664.5°
17	179.15	1.3698	130.79	659.2
99.5	80.66	1.2799	63.02	317.6
100	80.17	1.2794	62.66	315.8
110	72.29	1.2684	56.99	287.2
135	52.93	1.2412	42.64	214.9
179 *	28.38	1.1968	23.71	119.5

\* After ascertaining the rotation at 179°, the substance was allowed to cool down and readings were taken at 100°, these were found to be the same as before, showing that no decomposition had taken place at the higher temperature.

*Dimethyl Di-o-nitrobenzoyltartrate.*

The preparation was similar to that described for the other compounds. The acid chloride and dimethyl tartrate were heated at 160–200°. On distilling off the chloroform, as in the previous cases, a dark brown, resinous mass remained which was very soluble even in cold chloroform. In hot methylated spirit it was easily soluble, but separated as an oil on cooling. From benzene also it separates as an oil on the addition of light petroleum. Crystallisation was ultimately induced by allowing it to remain for a long time in contact with methylated spirit in an open vessel into which a small quantity of one of the other nitrobenzoyl compounds had been accidentally introduced. Crystallisation is more readily effected after the solution in methylated spirit has been filtered several times through animal charcoal.

*Rotation of Dimethyl Di-o-nitrobenzoyltartrate.*

Temp.	$\alpha_D$ for $l=1$ .	$d\ t^{\circ}/4^{\circ}$ .	$[\alpha]_D$ .	$[M]_D$ .
100°	– 132·10°	[1·3484]*	[– 97·97°]	[466·3]*
109 *	– 121·52°	[1·3454]*	[– 90·32 ]	[429·9]*.

As the dimethyl di-*o*-nitrobenzoyltartrate was not obtained in sufficient quantity to allow of complete observations on the fused substance, its rotation, and also that of the corresponding diethyl di-*ortho*-compound, were determined in benzene solution for comparison.

A 0·8555 per cent. solution of dimethyl di-*o*-nitrobenzoyltartrate in benzene gave :

$$\alpha_D = -1·41^{\circ}, d11^{\circ}/4^{\circ} = 0·8874, t = 11^{\circ}, l = 100·45 \text{ mm.}$$

$$[\alpha]_D^{11^{\circ}} = -184·90^{\circ}, [M]_D^{11^{\circ}} = -880·1^{\circ}.$$

A 0·8064 per cent. solution of diethyl di-*o*-nitrobenzoyltartrate in benzene gave :

$$[\alpha]_D = -0·86^{\circ}, d11^{\circ}/4^{\circ} = 0·8881, t = 11^{\circ}, l = 100·45 \text{ mm.}$$

$$[\alpha]_D^{11^{\circ}} = -119·55^{\circ}, [M]_D^{11^{\circ}} = -602·5^{\circ}.$$

Thus, as was to be anticipated, the methyl has a much higher molecular rotation than the ethyl compound.

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\* As through lack of material no density determinations could be made, the corresponding densities of the meta-compound have been used for the approximate calculation of the molecular rotation. These approximate figures have, therefore, been enclosed in brackets.

CLIX.—*The Decomposition of Methylcarbamide.*

By CHARLES EDWARD FAWSITT, D.Sc., Ph.D., Carnegie  
Research Fellow.

THE author has already shown (*Zeit. physikal. Chem.*, 1902, **41**, 601) that carbamide is decomposed by acids according to the law which holds good for reactions of the first order. This is due to the fact that the carbamide is first decomposed to a small extent into ammonium cyanate, this change taking place at a measurable rate, and, if the inverse change is neglected, according to the law governing reactions of the first order. The ammonium cyanate is decomposed into the ammonium salt of the acid used and carbon dioxide at a very much greater rate than that at which the ammonium cyanate is formed, and thus the rate of decomposition of carbamide by hot acids is almost identical with the rate at which carbamide is transformed into ammonium cyanate. Carbamide is decomposed by strong alkalis mainly on account of its conversion into ammonium cyanate. This salt is decomposed by the alkali, but at a much slower rate than that at which ammonium cyanate is decomposed by acids. Carbamide is, however, also directly hydrolysed to some extent by the strong alkalis.

The decomposition of carbamide into ammonium carbonate when heated in aqueous solution is a very slow process and is probably entirely due to the decomposition of the ammonium cyanate which is the first product of the change.

It was considered advisable to extend the investigations to the closely related alkylcarbamides, and the present paper deals with the decomposition of methylcarbamide.

*Theory of the Decomposition of Carbamides.*

As the theory set forth in a former paper (*loc. cit.*) concerning the decomposition of carbamide is corroborated by the results of the present paper on methylcarbamide, there seems to be little doubt that it is applicable to all the alkylcarbamides. These substances, when heated with water, decompose to a certain extent into the corresponding cyanates, this reaction terminating after heating for a few hours at the boiling point, when equilibrium is established between the carbamide and the cyanate. The velocity of the reaction before equilibrium is established is given by the equation:

$$dx/dt = k(A - x) - k'x^2 \dots (1),$$

where  $A$  is the concentration of the carbamide at the beginning of

the reaction,  $x$  the concentration of the cyanate in solution,  $t$  the time in minutes, and  $k, k'$  the velocity constants for the reactions carbamide  $\rightarrow$  cyanate and cyanate  $\rightarrow$  carbamide respectively. The velocity at the beginning of the reaction is given by the equation

$$dx/dt = kA \dots (2),$$

and the reaction stops when

$$k(A - x) = k'x^2 \dots (3).$$

Any further decomposition than that given by equation (3) can only take place if (a) the cyanate decomposes, or (b) the carbamide is directly decomposed into carbonate. The decomposition does proceed beyond the equilibrium point when the carbamide is heated with acids, alkalis, or even with water, and the results of experiment seem to indicate that in all cases the subsequent decomposition is due to the cyanate decomposing, although in the case of strong alkalis some direct saponification takes place.

In the case of strong acids, the variable  $x$  in the equation (1) vanishes so rapidly that the term  $k'x^2$  may be neglected, and the equation representing the velocity of reaction becomes

$$dx/dt = k(A - x) \dots (4).$$

This is the differential equation for a reaction of the first order, and the experimental results fully confirm this. As the constant  $k$  of the equation is also obtainable from the integral, a means is thus obtained of determining the velocity-coefficient of a reaction in one direction when there is an inverse change, namely, by destroying the products of reaction as soon as they are formed.

At the same time, the constant  $k$  obtained from experiments of this kind may not be quite the true value of this quantity. In the present instance, the assumption that in the presence of acid the cyanate is at once destroyed is not quite true, that is,  $k'x^2$  does not vanish altogether. Also, the constant  $k$  would in the present instance have to be corrected owing to the fact that  $A$  does not represent the whole concentration of the carbamide in solution, but, as the experiments show, only that part of the base which is free as contrasted with the portion combined with the acid.

In the case of the decomposition with water only, the term  $k'x^2$  diminishes as the cyanate decomposes into carbonate, and as the velocity of this change is small, the velocity with which the decomposition as a whole goes on is also small.

In the decomposition by alkali, we have a rate of decomposition of the cyanate, and consequently of the carbamide, intermediate between the rates with water and with acids, but superimposed on this is a

direct action of the alkali on the carbamide, so that with high concentrations of alkali a greater rate of decomposition is obtained than by the use of acids.

These conclusions are based on experiment and are of interest in so far as preconceived ideas of the decomposition of this series of substances would probably have led to the supposition that in the case of decomposition by acid or alkali a direct hydrolysis takes place.

#### EXPERIMENTAL.

The methylcarbamide (Kahlbaum's), when recrystallised from a mixture of ether and alcohol, melted at  $101^{\circ}$ , this melting point remaining unchanged on further crystallisation. The distilled water used in making the solutions had a specific conductivity of about  $4 \times 10^{-6}$ . As the reactions involved in the decomposition of carbamide were not affected by the kind of water used, ordinary (selected) distilled water was considered to be sufficiently pure for the purpose.

The reagents were enclosed in sealed tubes of steamed Jena glass with the exception of the alkaline solutions, which were placed in platinum tubes enclosed in sealed glass tubes.

The temperature of reaction was  $97.8^{\circ}$ , unless otherwise stated, and the tubes were kept at this temperature by placing them in a thermostat which contained water covered with a layer of melted paraffin wax to prevent evaporation.

The rate of reaction was ascertained by titrating the solution, if acid, with standard barium hydroxide, using methyl-orange as indicator, or, when alkaline, the tubes were opened below the surface of a known excess of acid, and then the excess of acid which remained was titrated with barium hydroxide. That this method is satisfactory is seen in the regularity of the curves representing the course of reaction in almost any of the following experiments, and also in the fact that the end-point as obtained by the titration method corresponds with the total decomposition of the methylcarbamide.

The time during which each tube was heated was corrected by the method already described (*Zeit. physikal. Chem.*, 1902, 41, 604). The velocity constants given throughout this paper are those calculated according to the formula

$$k = \frac{1}{t} \log_{10} \frac{A}{A-x},$$

$$\text{instead of } k = \frac{1}{t} \log_e \frac{A}{A-x},$$

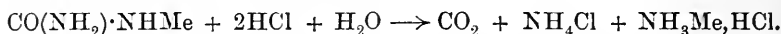
the real integral of equation (4).

A semi-molecular solution of methylcarbamide is taken as being

normal, since a molecular proportion of this amide (after decomposition) neutralises two equivalents of hydrochloric acid.

*The Action of Acids on Methylcarbamide.*

By analogy with carbamide, we should suppose that the reaction may be represented by the equation :



To test this, several grams of methylcarbamide were heated at  $98^\circ$  in a test-tube covered with paraffin for 14 days, and the contents were then allowed to cool ; some crystals separated out, but not in sufficient quantity to be analysed. The mother liquor was treated with alcohol and evaporated to a small bulk ; a large crop of crystals then separated, the chlorine in these being estimated by Volhard's method.

0.2274 gram of dried crystals required 0.708 gram of  $\text{AgNO}_3$ .

Ammonium chloride requires 0.722 gram of  $\text{AgNO}_3$ .

The mother liquor obtained, after filtering off this last crop of crystals, was evaporated, when more crystals separated ; these were discarded, and the residual mother liquor evaporated on the water-bath and then dried in a vacuum desiccator over sulphuric acid.

0.1467 gram required 0.377 gram of  $\text{AgNO}_3$ .

Methylamine hydrochloride required 0.369 gram of  $\text{AgNO}_3$ .

The products are therefore ammonium chloride, methylamine hydrochloride, and carbon dioxide, which is evolved in bubbles as soon as the reaction begins.

Nearly all the experiments were performed in duplicate, and therefore  $A - x_{(1)}$  and  $A - x_{(2)}$  are two independent determinations,  $A - x_{(m)}$  being the mean.

TABLE I.

N/16 Methylcarbamide and N/8 Hydrochloric Acid.

Time.	$A - x_{(1)}$ .	$A - x_{(2)}$ .	$A - x_{(m)}$ .	$k \times 10^5$ .
0'	10.65	10.65	10.65	—
90	9.74	—	9.74	43
175	8.88	8.89	8.89	44
256	8.36	—	8.36	41
373	7.40	7.52	7.46	41
428	7.22	—	7.22	39
972	4.23	4.40	4.32	40
1620	2.04	—	2.04	44

TABLE II.

*N*/16 Methylcarbamide and *N*/16 Hydrochloric Acid.

Time.	$A - x_{(1)}$ .	$A - x_{(2)}$ .	$A - x_{(m)}$ .	$k \times 10^5$ .
0'	10.76	10.76	10.76	—
179	8.98	9.02	9.00	43
245	8.42	—	8.42	43
308	8.07	8.12	8.10	40
514	6.64	6.68	6.66	41
834	4.97	—	4.97	40
1437	2.55	—	2.55	44

As in the case of carbamide, variation in the concentration of the acid in these dilute solutions makes no difference to the velocity of the decomposition.

TABLE III.

*N*/8 Methylcarbamide and *N*/8 Hydrochloric Acid.

Time.	$A - x_{(1)}$ .	$A - x_{(2)}$ .	$A - x_{(m)}$ .	$k \times 10^5$ .
0'	10.77	10.77	10.77	—
192	9.08	—	9.08	39
528	6.58	6.72	6.65	41
861	4.94	—	4.94	39
1365	2.87	2.97	2.93	41

TABLE IV.

*N*/8 Methylcarbamide and *N*/16 Hydrochloric Acid.

Time.	$A - x_{(1)}$ .	$k \times 10^5$ .
0'	10.77	—
110.5	9.64	44
198	8.89	42
253	8.37	43
502	6.61	42

TABLE V.

*N*/8 Methylcarbamide and *N*/32 Hydrochloric Acid.

Time.	$A - x$ .	$k \times 10^5$ .
0'	10.77	—
123	9.57	40
159	9.29	40
219	8.86	39

TABLE VI.

*N*/8 Methylcarbamide and *N*/4 Hydrochloric Acid.

Time.	$A - x$ .	$k \times 10^5$ .
0'	10.76	—
155	9.54	34
259	8.84	33
433	7.69	34
952	5.10	34
1667	2.90	34

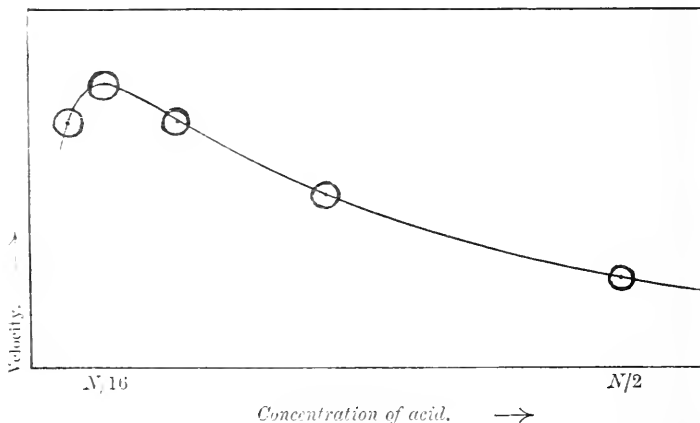
TABLE VII.

*N*/8 Methylcarbamide and *N*/2 Hydrochloric Acid.

Time.	$A - x$ .	$k \times 10^5$ .
0	10.76	—
199	9.46	28
304	8.94	26
462	8.08	27
592	7.44	27
830	6.40	27
1351	4.67	27

Whereas the change in the concentration of methylcarbamide from  $N/16$  to  $N/8$  does not appreciably affect the velocity constant so long as the concentration of hydrochloric acid is not altered, and although the change of concentration of the latter within certain limits does not greatly change the velocity constant, yet the more highly concentrated acid apparently diminishes the rate of reaction considerably. This result is best shown by the curve. A maximum occurs at the point corresponding with the mixture ( $N/8$  methylcarbamide +  $N/16$  hydrochloric acid); this relation is exactly similar to that found in the case of carbamide, and it is capable of a similar explanation. The methylcarbamide, just like carbamide, combines with hydrochloric acid and forms the compound  $\text{CO}(\text{NH}_2) \cdot \text{NH} \cdot \text{CH}_3, \text{HCl}$ .

In aqueous solution, this compound is decomposed into methylcarb-



amide and hydrochloric acid to a very considerable extent, and it is only the free methylcarbamide which undergoes decomposition at any instant. The equilibrium between the concentrations of the free acid and the free methylcarbamide is given by the equation :

$$\frac{C_{\text{Base}} \times C_{\text{Acid}}}{C_{\text{Salt}}} = K \quad . \quad . \quad (5),$$

where  $C$  represents the concentration of the substance and  $K$  is a constant. As  $C_{\text{Acid}}$  increases,  $C_{\text{Base}}$  diminishes, and this is the reason for the decrease in the velocity of decomposition and for the apparent decrease in the velocity-coefficient as  $C_{\text{Acid}}$  is increased. To show that the relationship (5) holds for these experiments, one may assume that the solution ( $N/8$  methylcarbamide and  $N/16$  hydrochloric acid, Table IV) contains 8 per cent. of the base as salt. Then the calculated per-

centages of free methylcarbamide in the acid solutions of Tables III, VI, and VII are 85, 74, and  $57\frac{1}{2}$  per cent. respectively.

These values would correspond with the velocity constants 41, 35, 27, to which the experimental numbers 40, 34, 27 approximate very closely.

As  $C_{\text{Acid}}$  is decreased,  $C_{\text{Base}}$  increases until the base and acid are in molecular proportion,  $\text{CO}(\text{NH}_2)\text{NH}\cdot\text{CH}_3\cdot\text{HCl}$ . After this proportion is reached, the increase continues, although more slowly than before, and it might be expected therefore that the velocity constant would be greatest in the most dilute acid solutions. It appears, however, that the rate of decomposition of methylamine cyanate to methylamine hydrochloride is not altogether independent of the concentration of acid, but is less in the more dilute acid solutions. It is due to this circumstance that the rate of decomposition of methylcarbamide by the very dilute acids is less than the value obtained when the acid is used in  $N/16$  solutions.

An experiment with a more concentrated solution of methylcarbamide gave the following results.

TABLE VIII.

$N/2$  Methylcarbamide and  $N/2$  Hydrochloric Acid.

Time.	$A - x$ .	$k \times 10^5$ .
0'	8.65	—
356	6.76	30
858	4.80	30
1040	4.19	30
1126	3.89	31
1301	3.44	31
1558	2.77	32

The velocity constant increases somewhat as the reaction proceeds, exactly as in the case of carbamide, this being due to the relatively greater amount of free methylcarbamide present in the solution as the acid becomes neutralised.

An experiment was tried using hydrobromic acid instead of hydrochloric acid, with the following result (compare Table III) :

TABLE IX.

$N/8$  Methylcarbamide and  $N/8$  Hydrobromic Acid.

Time.	$A - x_{(1)}$ .	$A - x_{(2)}$ .	$A - x_{(m)}$ .	$k \times 10^5$ .
0'	13.71	13.74	13.73	—
252	10.94	11.01	10.97	39
438	9.33	9.40	9.36	38
607	8.07	8.14	8.10	38
823	6.54	6.60	6.60	39

The numbers show that, within the limits of experimental error, the velocity is the same as that obtained with hydrochloric acid. Hydrobromic and hydrochloric acids are of approximately the same strength, but sulphuric acid is weaker and might be expected to give different results.

As in the case of carbamide, smaller numbers were obtained for the velocity-coefficient with sulphuric acid than with hydrochloric acid.

TABLE X.

*N*/16 Methylcarbamide and *N*/16 Sulphuric Acid.

Time.	$A - x_{(1)}$ .	$A - x_{(2)}$ .	$A - x_{(m)}$ .	$k \times 10^5$ .
0'	10.79	10.79	10.79	—
161	9.42	9.51	9.47	35
303	8.34	—	8.34	37
949	4.58	4.64	4.61	39
1445	2.86	—	2.86	40

The constants are all smaller than with hydrochloric acid, and increase during the reaction just as in the case of carbamide, this being undoubtedly due to the slower decomposition of the cyanate by sulphuric acid.

These experiments show that the results obtained in the decomposition of carbamide and methylcarbamide by acids are very similar, the only difference being that the reaction in the case of the latter compound is slower than in that of the former. The foregoing experiments were conducted at  $97.8^\circ$ , and therefore an additional determination of the velocity constant for methylcarbamide was made at  $99.2^\circ$ , this being the temperature employed in the case of carbamide.

TABLE XI.

*N*/8 Methylcarbamide and *N*/8 Hydrochloric Acid.

Time.	$A - x$ .	$k \times 10^5$ .
0'	10.72	—
103	9.56	48
159	8.97	49
210	8.40	50
368	7.16	48
423	6.80	47
969	3.88	49
4042	0.30	—

The average value of the velocity constant is 48.5, being almost exactly one-half of the constant 101 obtained for carbamide.

Walker and Appleyard found (Trans., 1896, 69, 193) that the velocity constant  $k$  in our equation as calculated from a determination of  $k'$  and  $K$  (the equilibrium constant) was 0.000038 at  $59.6^\circ$  for

carbamide and 0.000022 at the same temperature for methylcarbamide, the ratio between the two velocities being almost exactly as in my experiments. I have measured the velocity of decomposition of methylcarbamide by acids at 59.6° with the following results:

TABLE XII.

*N*/8 Methylcarbamide and *N*/8 Hydrochloric Acid.

Time.	$A - x.$	$k \times 10^7.$	$\frac{k \times 10^7.}{0.4343}$ Average.
0'	9.63	—	} 53
5415	9.33	25	
18390	8.83	20	
38880	7.90	22	
41850	7.74	23	

The velocity constant obtained in this experiment is smaller than the value 0.000022. This is due to the following circumstances: (1) only the free methylcarbamide in solution is decomposing at any time; (2) the cyanate is not immediately decomposed by the acid; (3) the calculated value of  $k$  may not be the exact value of that quantity.

*The Decomposition of Methylcarbamide in Aqueous Solution.*

The decomposition of methylcarbamide takes place in aqueous solution in accordance with the equation  $\frac{dx}{dt} = k(A - x) - k'x^2$ .

Although we assume that the reaction starts at a rate very closely represented by the velocity-coefficient of the acid experiments, this rate decreases as  $x$  increases, and the reaction should cease at a point where there is approximately 96 per cent. of methylcarbamide still undecomposed. However, further decomposition into methylamine carbonate takes place, although this reaction goes on very slowly.

An experiment made to measure this rate gave the following results:

TABLE XIII.—*N*/8 Methylcarbamide.

Time.	$A - x.$
0'	10.00
146	9.58
1356	8.76
2970	7.73
5565	7.12

The reaction is therefore much slower than the corresponding change with carbamide.

*The Decomposition of Methylcarbamide by Alkalis.*

From the great similarity existing between the foregoing results and those previously obtained for carbamide, it should be possible to predict with considerable certainty what would happen in the case of the reaction with alkalis. Weak alkalis (ammonia, for example) having been found in the case of carbamide to give a velocity comparable to that observed with water alone, this case was not investigated, but experiments made with the strong alkalis gave the anticipated results.

TABLE XIV.

*N*/8 Methylcarbamide and *N*/8 Sodium Hydroxide.

Time.	$A - x$ .	$k \times 10^5$ .
0'	13.81	—
171	11.95	37
275	10.95	37
833	7.47	32

TABLE XV.

*N*/2 Methylcarbamide and *N*/2 Sodium Hydroxide.

Time.	$A - x_{(1)}$ .	$A - x_{(2)}$ .	$A - x_{(m)}$ .	$k \times 10^5$ .
0'	10.00	10.00	10.00	—
173	8.33	8.50	8.41	44
242	7.77	7.81	7.79	44
456	6.21	6.22	6.21	45
788	4.70	4.85	4.78	41
1032	3.98	4.20	4.09	38
4020	0.75	—	—	—

TABLE XVI.

*N*/2 Methylcarbamide and 3*N*/2 Sodium Hydroxide.

Time.	$A - x_{(1)}$ .	$A - x_{(2)}$ .	$A - x_{(m)}$ .	$k \times 10^5$ .
0'	10.00	10.00	10.00	—
93	8.73	8.74	8.74	63
244	6.70	7.10	6.90	66
312	6.36	—	6.36	63
689	3.51	3.52	3.51	66

It is possible, by using a high concentration of alkali, to get a velocity greater than that obtained with acids. There is little doubt that some direct hydrolysis takes place in addition to the indirect decomposition, although it is scarcely possible to calculate the constants for the second order owing to the complication introduced by the indirect action. That the decomposition is due to the OH' ions is brought out by the fact that potassium hydroxide has almost exactly the same effect as sodium hydroxide (compare Table XV).

TABLE XVII.

*N*/2 Methylcarbamide and *N*/2 Potassium Hydroxide.

Time.	$A - x_{(1)}$ .	$A - x_{(2)}$ .	$A - x_{(m)}$ .	$k \times 10^5$ .
0	10.00	10.00	10.00	—
194	8.32	8.38	8.35	40
319	7.40	—	7.40	41
668	4.88	4.90	4.89	46
7720	0.35	—	—	—

In the hydrolysis of esters and amides by acids and alkalis, it is generally found that the action of alkalis is much greater than that of acids, but in the case of carbamide and its derivatives, even the most concentrated alkali hydrolyses the compounds with difficulty, and it might therefore be concluded that the direct action of acids on these substances at 100° is practically negligible. So far as one can judge from the experimental results, the whole of the action of acids on these substances is due to an indirect decomposition taking place after the isomeric transformation.

*Summary of Results.*

(1) In its decomposition on treatment with acids, alkalis, and water alone, methylcarbamide behaves very similarly to carbamide.

(2) The decomposition of methylcarbamide by acids is due to its transformation into methylamine cyanate, this salt being then decomposed by the acid. This transformation is a reaction of the first order.

(3) The method of destroying the reaction products in a case of dynamic isomerism may be used with advantage in certain reactions to obtain the velocity-coefficient of the transformation in one direction.

(4) The equilibrium  $\frac{C_{\text{CON}_2\text{H}_3\cdot\text{CH}_3} \times C_{\text{HCl}}}{C_{\text{CON}_3\text{H}_3\cdot\text{CH}_3, \text{HCl}}} = K$  is established by the experiments on the velocity of decomposition, as it is only the free methylcarbamide which gives the active concentration of substance decomposing at any instant.

(5) A direct hydrolysis of methylcarbamide is brought about only very slightly even by very concentrated alkali.

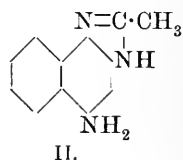
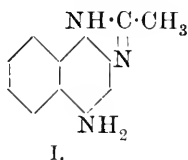
I desire to express my thanks to the Executive Committee of the Carnegie Trust for the Universities of Scotland and to the Trustees of the Earl of Moray Research Fund for defraying all expense connected with this investigation. I wish also to thank Professor Crum Brown for the interest which he has shown in my work.

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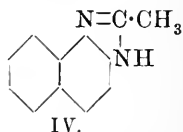
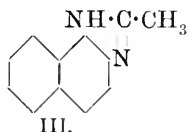
CLX.—*The Isomerism of the Amidines of the Naphthalene Series (Fifth Communication on Anhydro-bases).*

By RAPHAEL MELDOLA, F.R.S., and JOSEPH HENRY LANE.

THE isomeric aminoamidines described in previous communications (Trans., 1887, 51, 699; 1899, 75, 1011; 1900, 77, 1159; 1903, 83, 1185), and obtained from 2:4-dinitroaceto- $\alpha$ -naphthalide by reduction with tin and hydrochloric acid or with iron and hydrochloric acid respectively, can be represented on the view that they are structural isomerides by the formulæ:



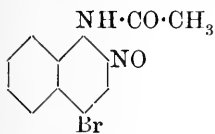
The corresponding amidines have the formulæ:



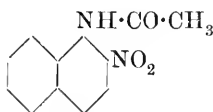
The experimental results made known in the present paper enable us to state that the base obtained by reduction with tin and acid (M. and S. base) has the formula I, and the ethenyldiaminonaphthalene derived from it by replacing the amino-group by hydrogen (Trans., 1903, 83, 1190) the formula III. Markfeldt's base is the  $\beta$ -NH-aminoamidine (formula II), and the corresponding ethenyldiaminonaphthalene (Prager's base; see Trans., 1900, 77, 1170, and 1903, 83, 1196) has the formula IV.

The evidence on which these conclusions are based has been obtained by a comparison of the *N*-alkyl derivatives prepared by the alkylation of the amidines with the *N*-alkyl bases prepared synthetically and of known constitution. By this method, it has been proved that the *N*-ethyl derivative obtained by the direct ethylation of the new ethenyldiaminonaphthalene (Trans., 1903, 83, 1193) is identical with a synthetical anhydro-base known to contain the *N*-ethyl-group in the  $\alpha$ -position. Prager's ethenyldiaminonaphthalene, on the other hand, gives an *N*-ethyl derivative (*ibid.*, 1197) which is identical with a synthetical base known to contain the *N*-alkyl in the  $\beta$ -position. The formula of the only ethenyldiaminonaphthalene (Prager's) known up

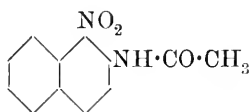
to the time of these researches cannot be inferred from its mode of formation, and different views have been held concerning its constitution. Thus Meyer and Jacobson, in their "*Lehrbuch der Organischen Chemie*" (Vol. II, Part 2, p. 352), assign the correct formula (No. IV, p. 1592). On the other hand, Otto Fischer, who obtained the same base by heating naphthylene-1:2-diamine with acetic acid and sodium acetate, assigns the  $\alpha$ -NH-formula (No. III, p. 1592; *Ber.*, 1901, 34, 934). As will be seen from the various modes of formation of this amidine, there must be isomeric transformation in the case of some of the processes, since, according to published statements, it is obtainable from the following compounds:



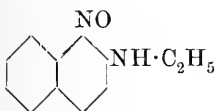
I.



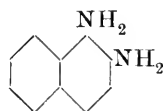
II.



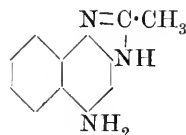
III.



IV.



V.



VI.

I. Prager, *Ber.*, 1885, 18, 2161.

II. Lellmann and Remy, *Ber.*, 1886, 19, 799.

III. Liebermann and Jacobson, *Annalen*, 1882, 211, 67.

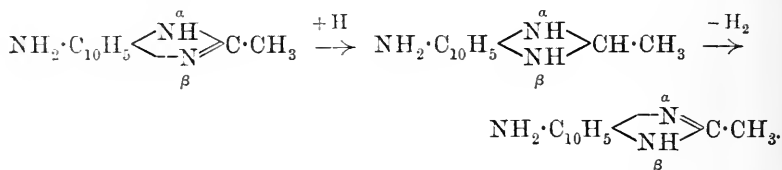
IV. O. Fischer and Hepp, *Ber.*, 1887, 20, 2472.

V. O. Fischer, *Ber.*, 1900, 34, 934.

VI. *Trans.*, 1900, 77, 1170; 1903, 83, 1196.

Since the same amidine is obtained by the reduction of such diverse compounds as those formulated over I, II, and III, it appears that the  $\beta$ -NH-position in the amidine ring is the more stable. This is in harmony with the observation that the M. and S. base can, by further reduction, be converted into the isomeride (*Trans.*, 1903, 83, 1200) whilst the reverse change cannot be effected. It might be expected, in accordance with this conclusion, that the new ethenyldiaminonaphthalene would by further reduction be converted into Prager's base. An experiment having this object in view led, however, to a negative result. The mechanism of the isomeric change in the case of the aminoamidines is still obscure and requires further investigation, the conversion of a compound into an isomeride by the action of nascent hydrogen being as yet without a parallel. The facts made known in this and in previous communications may be interpreted on the view that in the amidine ring the  $\beta$ -nitrogen atom has a greater degree of "unsatura

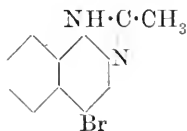
tion" than the  $\alpha$ -nitrogen atom. Thus, on reduction, the M. and S. base may be supposed to pass through a series of changes:



The addition of hydrogen so as to saturate the ring temporarily and its subsequent removal so as to form an unsaturated ring is quite in accordance with the well-known property of the amidine ring, namely, its inability to form a stable saturated dihydro-cycloid. The unsaturated character of the  $\beta$ -nitrogen atom in the substituted amidines of the type of the M. and S. base is evidently connected with the presence of a substituent in the para- $\alpha$ -position and is independent of the nature of the substituent. This is shown by the following considerations.

(A) The reduction of the M. and S. base by iron and hydrochloric acid results in the formation of Markfeldt's base. The para- $\alpha$ -group is present in this case. When this group is removed, the ethenyldiaminonaphthalene containing the  $\alpha$ -NH is sufficiently stable to resist the further action of reducing agents.

(B) The original source of Prager's ethenyldiaminonaphthalene was 4-bromo-2-nitroaceto- $\alpha$ -naphthalide (Formula I, p. 1593). This compound on reduction gives the bromo-anhydro-base:

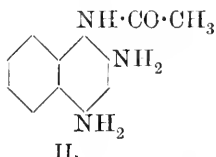
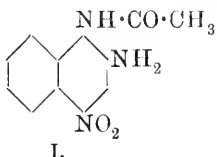


That this base has the above constitution is proved by its production from the M. and S. base by the diazo-method, as described in the present paper. On removal of the bromine by reduction, as in Prager's original method, the amidine ring undergoes transformation into the more stable  $\beta$ -NH-grouping.\* The mechanism of the change in this case may be supposed to be the same as that of the trans-

\* This last statement is based entirely on the supposition that Prager's ethenyldiaminonaphthalene is identical with that obtained by the other methods. There is no direct proof of this in that author's original paper of 1885, and it will be necessary to repeat the work in the light of the present results. There is no doubt about the identity of Prager's bromoamidine with that obtained from our aminoanhydro-base by the Sandmeyer process as mentioned above. This bromoanhydro-base was also independently obtained and described by one of the authors of this paper in 1885 (Meldola, Trans., 1885, 47, 506).

formation of the M. and S. base into Markfeldt's, namely, the addition and removal of hydrogen.

The method of producing isomeric aminoamidines made known in the course of these researches, namely, the action of different reducing agents on the same dinitro-compound, is, so far as we are aware, unique, and we propose extending the investigation into the benzene series in order to ascertain whether isomerisation can be brought about by the same method applied to compounds of analogous constitution in this series, such, for example, as the dinitroacetotoluidides. The explanation of the different action of the two reducing agents resolves itself, according to the interpretation of the results which we now venture to offer, into the general principle of the different orienting influence of a nitro-group and an amino-group respectively. Thus, if it be assumed that one of the reducing agents, probably the iron and hydrochloric acid, reduces the nitro-groups successively and that the other reducing agent attacks both nitro-groups simultaneously, the intermediate compounds would have the constitutions expressed by the formulæ :

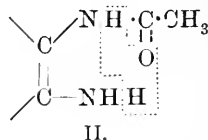
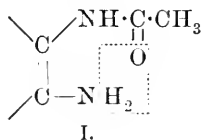


In I, the formation of the amidine ring takes place under the orienting influence of a nitro-group, whilst in II the ring is formed under the influence of an amino-group. The constitutions of the resulting rings, that is, the position of the imino-group with respect to the para- $\alpha$ -substituent, might under these circumstances be expected to be different.

The hypothesis which is now offered seems most in harmony with the experimental results hitherto obtained, although some direct evidence of the formation of the intermediate nitroamidine must be obtained before this explanation can be regarded as final. Experiments in this direction have already been made, but so far without success, the extreme insolubility of dinitroaceto- $\alpha$ -naphthalide in alcohol or other solvents making it impossible to get the compound into solution with tin or iron as reducing agent excepting as a completely reduced product, that is, as an aminoamidine. The research has not, however, been carried very far along this line and further experiments will be undertaken. We may mention that nickel and hydrochloric acid reduce the dinitro-compound but very slowly, the alcoholic solution requiring long boiling before complete solution is effected. The product is neither of the isomeric amino-

amidines and may consist of an intermediate compound, but it appears to be oxidisable and easily resinified, so that we have not hitherto succeeded in isolating it in a condition suitable for investigation.

According to the interpretation which we have given to the experimental results, the orienting influence of the substituent in the para- $\alpha$ -4-position may take practical effect by determining which hydrogen atoms are removed with the oxygen of the acetyl group. Thus, according to the schemes given below,



I represents the formation of the M. and S. base and II the formation of the isomeride. It is of interest to note that the constitutional formula originally assigned to the aminoamidine in 1887 (*Trans.*, 1887, 51, 700) is now confirmed by the discovery of Markfeldt's base and the determination of its constitution in the course of the present researches.

The peculiar action of iron as a reducing agent has been made further evident by an extension of the experiments described in the last communication (*Trans.*, 1903, 83, 1200). Thus, continued reduction of the M. and S. base with iron and hydrochloric acid converts this base, as already stated, into Markfeldt's isomeride. We have now found that this transformation is not brought about by the prolonged action of zinc and hydrochloric acid or of sodium amalgam and hydrochloric acid, the experimental conditions being the same as those under which the iron and acid effect the change in question. Prolonged heating with zinc dust and sodium hydroxide solution also failed to convert the M. and S. base into its isomeride. Aluminium and hydrochloric acid reduce the dinitro-compound with the formation of our (M. and S.) base.

Before proceeding to give details of our later experiments, we desire to place on record our indebtedness to Dr. Markfeldt, who, being unable to carry on the work himself, has been good enough to communicate to us all his unpublished results. These will be acknowledged and included in their respective places in due course. It appears from the notes submitted that the free M. and S. base described in the last communication (*loc. cit.*, p. 1185) was also independently obtained by him in 1900 by basifying the pasty sulphate with ammonium carbonate and strong caustic soda solution.

## EXPERIMENTAL.

*Oxidation of the Aminoamidines.*

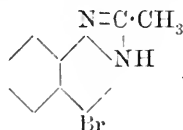
The sulphate of the M. and S. base was basified by an excess of sodium hydroxide, and the hot alkaline solution treated with a solution of potassium permanganate until a distinct red colour showed that the oxidising agent was present in excess. After removal of the excess of permanganate by means of ferrous sulphate and filtration, the filtrate was evaporated to a small bulk and acidified with sulphuric acid. A resinous substance which separated out at this stage was filtered off and the clear solution extracted with ether. The ethereal extract, on evaporation, gave a large quantity of phthalic acid, which was identified by the usual tests. Markfeldt's base (sulphate), submitted to a similar treatment, gave the same result. The resin obtained as a by-product of oxidation by alkaline permanganate is an acid substance dissolving in aqueous alkali. It could not be obtained as a definite compound, and was not further examined; it gave a sublimate of phthalic anhydride on heating in a dry tube. The large yield of phthalic acid from both bases leaves no doubt that they are homonuclear naphthalene derivatives, and that in neither case is there condensation between the hydrocarbon nuclei.

*Replacement of the Amino-group in the Isomeric Ethenyltriamino-naphthalenes by Bromine.*

The pasty sulphate of the  $\alpha$ -NH-aminoamidine (M. and S. base) was diazotised in the usual way and the diazonium salt decomposed by heating with an excess of cuprous bromide until nitrogen ceased to be evolved. The base was extracted from the resinous product by means of alcoholic sodium hydroxide, the solution filtered to remove copper compounds, the alcohol distilled off, and the solution neutralised with acetic acid. On cooling, the base separated out in crystalline crusts. When dry, it melts at  $230^{\circ}$  with previous softening. A study of the properties of this compound served to show that it was identical with the bromoethenyldiaminonaphthalene obtained by Prager and by Meldola in 1885 (*Ber.*, 1885, 18, 2161; *Trans.*, 1885, 47, 506), the constitutional formula of which has been given in the preceding part of this paper. The tendency of the salts of this base to separate in a gelatinous form is especially characteristic. We may also add that it shows markedly acid properties by virtue of the imino-group of the amidine ring dissolving, especially when freshly precipitated, in aqueous ammonia or sodium hydroxide and being precipitated on neutralisation of the solution with acid. The insolubility of the nitrate which was observed in the product obtained

by this diazo-method has already been recorded (Meldola, *loc. cit.*). This bromoanhydro-base does not yield a definite picrate. No precipitate is formed on mixing concentrated alcoholic solutions of the base and picric acid. Dilution with water caused the precipitation of a yellow, amorphous product which gave no definite result on analysis. It appeared to be a mixture of picric acid and base, from which the picric acid was gradually removed by successive attempts at purification, and it was not further examined.

The introduction of bromine into the isomeric  $\beta$ -NH-aminoamidine (Markfeldt's base) was effected in the same way and the extraction carried out as above. The base thus obtained proved to be uncrystallisable and yielded no distinctly characteristic compounds. It is, however, unquestionably isomeric with the above bromoanhydro-base, from which it differs most markedly by giving an immediate precipitate on the addition of an alcoholic solution of picric acid to an alcoholic solution of the base. The isomeride, as already stated, gives no precipitate under these circumstances. The picrate of the new bromoethenyldiaminonaphthalene is not, however, a very definite compound. It separates from a hot alcoholic solution on cooling in a flocculent state and could not be crystallised from any solvent. From its mode of formation, this bromoamidine must have the formula :



The base possesses in a remarkable degree the property of forming salts which are insoluble in presence of an excess of acid. If, for example, the freshly precipitated gelatinous base is dissolved in just sufficient dilute hydrochloric acid to form a clear solution, the addition of even a slight excess of acid causes an immediate precipitation of a gelatinous hydrochloride. The nitrate is particularly insoluble in presence of free nitric acid, and the base was in fact purified by first precipitating as nitrate, collecting, washing with dilute nitric acid, and finally basifying by ammonium carbonate. None of the salts or double salts appear to be crystallisable. The hydrochloride, nitrate, and sulphate, when boiled with water, yield a resin which is probably the free base resulting from the dissociation of the salt by hot water. On the whole, the compound may be described as being more distinctly basic and less acid than its isomeride. The platinichloride and aurichloride were both prepared and proved to be gelatinous, non-crystallisable, and highly hydrated compounds which gave unsatisfactory results on analysis. When dry, these double salts are brittle dark resins.

*Further Study of the  $\alpha$ -N-Ethylethenyldiaminonaphthalene.*

This compound has already been described at some length in our last paper (Trans., 1903, 83, 1193), but in view of the important part which it has played in determining the constitution of these bases its investigation has been continued and the results are now given.

*Determination of the Molecular Weight.*—A specimen of the base was prepared by ethylating the ethenyldiaminonaphthalene (*loc. cit.*, 1190) by heating it with a little more than the calculated quantity of ethyl iodide (diluted with alcohol) in a sealed tube for five hours at  $100^{\circ}$ . The crystalline hydriodide was basified and the base purified by alternate acid and alkaline treatment in the manner already described. The product proved to be identical with that obtained by the ethylation of the *N*-silver salt. The specimen used for the determination of the molecular weight was purified by successive crystallisation from (1) a mixture of benzene and petroleum, (2) carbon disulphide, (3) ether, in all of which it dissolves quite readily. The crystals deposited by the slow spontaneous evaporation of the ethereal solution consisted of large, colourless, transparent tablets. The melting point was  $85^{\circ}$ .

0.1031 gave 11.6 c.c. moist nitrogen at  $10^{\circ}$  and 750 mm.  $N = 13.13$ .

$C_{14}H_{14}N_2$  requires  $N = 13.3$  per cent.

0.2078 dissolved in 21.55 benzene gave  $\Delta t$   $0.23^{\circ}$ . M. W. = 209.6.

0.2026     "     "     23.99     "     "     "     0.20 $^{\circ}$ . M. W. = 211.3.

$C_{14}H_{14}N_2$  requires M. W. = 210.

This result leaves no doubt that the compound and therefore the corresponding ethenyl-diamino- and -triamino-naphthalenes are monomolecular compounds and that no nuclear condensation takes place on reducing 2:4-dinitroaceto- $\alpha$ -naphthalide with tin and hydrochloric acid.

*Salts of  $\alpha$ -N-Ethylethenyldiaminonaphthalene.*—To the information published in the last paper we are able to add the following.

The *picrate* (*loc. cit.*, p. 1194), which melts with decomposition at  $234$ — $235^{\circ}$ , is an extraordinarily stable compound, resisting decomposition by caustic alkali or dilute mineral acids, even when boiled with these reagents. The *oxalate* and *citrate* were obtained as uncrystallisable syrups.

The *nitrate*\* is a very characteristic salt, crystallising from hot water on cooling in rosettes of straw-coloured needles. The salt dried

\* The nitrate of the  $\alpha$ -NH-ethenyldiaminonaphthalene (that is, the unalkylated base) was also prepared. It was obtained as an amorphous, yellow powder which, after drying in the water-oven, gave results corresponding with the formula  $C_{12}H_{10}N_2, HNO_3, 1\frac{1}{2}H_2O$ .

at the ordinary temperature under a desiccator lost practically nothing on drying in the water-oven, specimens so dried giving the following results on analysis :

0.1021 gave 12.4 c.c. moist nitrogen at  $11^{\circ}$  and 765 mm.  $N = 14.38$ .

0.1240 „ 15.2 c.c. „ „ „ „  $11^{\circ}$  „ 767 mm.  $N = 14.56$ .

$C_{14}H_{14}N_2, HNO_3, H_2O$  requires  $N = 14.46$  per cent.

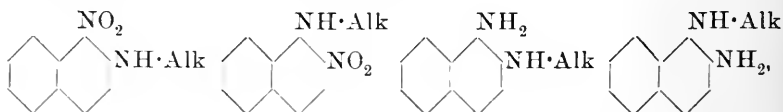
0.50 reduced in alkaline solution with coppered zinc foil gave ammonia corresponding with  $0.1077 HNO_3 = 21.54$  per cent.

$C_{14}H_{14}N_2, HNO_3, H_2O$  requires  $HNO_3 = 21.64$  per cent.

The water could not be expelled on heating in an air-bath without decomposition of the salt.

*Syntheses of the N-Alkylamidines of the Naphthalene Series.*

The isomeric *N*-alkylamidines having been obtained and characterised, it remained only to ascertain the position of the *N*-alkyl group in the amidine ring in order to determine the constitution of the two isomerides. It is evident that this problem could have been solved by preparing compounds of the types :



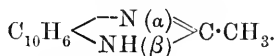
and converting these into anhydro-bases by the usual methods. The practical difficulties which were encountered in attempting to find suitable methods for the preparation of such compounds were, however, far greater than was anticipated, and a large amount of experimental work leading to negative results had to be carried out before satisfactory processes were discovered. These difficulties will be mentioned in the order in which they were encountered, since, although the results were negative so far as our particular object was concerned, they are of interest as giving in many cases new and striking examples of the special properties of naphthalene derivatives.

The first experiments were undertaken with the object of preparing mono-alkyl derivatives of  $\beta$ -naphthylamine,\* a supply of ethyl- $\beta$ -naphthylamine having been kindly placed at our disposal by Dr. G. T. Morgan. This compound was acetylated and many attempts made to prepare the  $\alpha$ -nitroethylaceto- $\beta$ -naphthalide by nitration under various conditions. All these attempts failed, the nitration not taking place at all or else going too far. The "protective" influence of the alkyl

\* This part of the work was carried out with the assistance of Mr. John Vargas Eyre, who was, however, obliged to leave the College before its completion.

group is in this case so marked that the  $\alpha$ -ortho-position appears to be unattackable.

An attempt was next made to prepare 2-ethylnaphthylene-1:2-diamine by the reduction of benzeneazoethyl- $\beta$ -naphthylamine. The azo-compound, which was first described by Henriques (*Ber.*, 1884, 17, 2669), was prepared in the usual way by combining diazotised aniline with ethyl- $\beta$ -naphthylamine. Reduction was effected by dissolving the azo-compound in glacial acetic acid, adding excess of zinc dust and a few drops of sulphuric acid to start the reaction, and boiling until the solution had become colourless. After filtration, the solution was boiled for some hours with the addition of a little acetic anhydride, then evaporated to a small bulk, and the product redissolved in dilute hydrochloric acid. On adding ammonia, the base separated as an oil, which was washed free from inorganic salts and purified by repeated solution in oxalic acid and reprecipitation by alkali. The resinous base thus obtained gave a picrate melting when pure at  $248^\circ$  and having all the properties of the *N*-ethyl derivative of Prager's ethenyl-diaminonaphthalene described in our last paper (*Trans.*, 1903, 83 1197). The constitution of the last base is thus shown to be



The yield of  $\beta$ -ethylnaphthylene-1:2-diamine by this method is extremely small, the benzeneazo-compound not being a suitable source of this alkyldiamine, a fact apparently known to Otto Fischer, who used the *p*-sulphobenzeneazo-compound for this purpose (*Ber.*, 1893, 26, 193). The reduction of the benzeneazo-compound by zinc dust and acetic acid appears to give rise, as the chief product, to a non-basic oily compound, which may be a hydrazo-compound. This oily product of reduction, not having any immediate bearing on the problem under investigation, has not been further examined. We may place on record, however, the observation that the same oily product is obtained by reducing the azo-compound in alcoholic solution with zinc dust and hydrochloric acid. Reduction with tin and hydrochloric acid appears to result in a "benzidine" or "semidine" transformation, so that this method had also to be abandoned. The preparation of the alkyldiamine on a larger scale by Otto Fischer's method was, however, at this stage rendered unnecessary by the discovery of a direct process for the synthesis of the compound required.

*Preparation of  $\alpha$ -Nitroalkyl- $\beta$ -naphthylamines and Reduction of their Acetyl Derivatives.*

$\beta$ -Naphthyl methyl and ethyl ethers were prepared in the usual way by boiling  $\beta$ -naphthol with the alcohol and a little sulphuric acid.

The ethers, after purification, were converted into mononitro-derivatives by nitration in cooled glacial acetic acid with one molecular proportion of fuming nitric acid largely diluted with acetic acid. The 1-nitro- $\beta$ -naphthyl ethyl ether has been described by Wittkampff (*Ber.*, 1884, 17, 394), and the corresponding methyl ether by W. A. Davis (*Proc.*, 1896, 12, 231). These ethers are readily converted into 1-nitromethyl- $\beta$ -naphthylamine by heating with an alcoholic solution of methylamine in a sealed tube at 160—170° for 10 hours. The ethyl ether gives the better result, the ethoxy-group being the more readily displaceable.

1-Nitromethyl- $\beta$ -naphthylamine,  $C_{10}H_6 \begin{smallmatrix} \text{NO}_2^{(1)} \\ \text{N} \end{smallmatrix} \cdot \text{CH}_3^{(2)}$ , crystallises from glacial acetic acid in beautiful, red, prismatic needles melting, when pure, at 124—125°; it is only feebly basic.

0.1318 gave 16.25 c.c. moist nitrogen at 23° and 761.3 mm.  $N = 13.90$ .  
 $C_{11}H_{10}O_2N_2$  requires  $N = 13.86$  per cent.

The nitrosoamine,  $C_{10}H_6 \begin{smallmatrix} \text{NO}_2^{(1)} \\ \text{N}(\text{NO}) \end{smallmatrix} \cdot \text{CH}_3^{(2)}$ , obtained by adding solid sodium nitrite to a cold saturated solution of the nitromethylnaphthylamine in glacial acetic acid, crystallises from alcohol in long, straw-coloured needles melting at 100°.

0.1031 gave 16.1 c.c. moist nitrogen at 17.7° and 759.7 mm.  $N = 18.03$ .  
 $C_{11}H_9O_3N_3$  requires  $N = 18.18$  per cent.

The acetylation of this nitromethylnaphthylamine takes place only slowly, many hours' boiling with excess of acetic anhydride and dry sodium acetate being necessary before the conversion is complete. The acetyl derivative was isolated by diluting the acetic anhydride solution with water, evaporating off the excess of acetic acid, and neutralising the residual liquor with ammonia. The compound separates out as an oil, which slowly solidifies. After being washed with water and crystallised from dilute alcohol until the melting point was constant, the pure compound was obtained in the form of pale greenish-yellow, glistening scales melting at 112—113°.

0.0992 gave 9.5 c.c. moist nitrogen at 14° and 770.4 mm.  $N = 11.41$ .  
 $C_{13}H_{12}O_3N_2$  requires  $N = 11.49$  per cent.

The acetyl derivative was reduced by adding it in small portions to a hot solution of stannous chloride in presence of tin and hydrochloric acid. A crystalline stannichloride separates out as the reduction proceeds if the solution is kept in a concentrated condition. The hydrochloride of the base was liberated in the usual way by the action of sulphuretted hydrogen, and, after removal of the tin, the solution was evaporated to a small bulk, and the crystalline pulp of the hydro-

chloride thus obtained basified with ammonia. The resinous base thus liberated was purified by solution in aqueous oxalic acid, filtration, and reprecipitation by alkali, this process being repeated until the base dissolved in dilute oxalic acid without leaving any residue. The base, after crystallisation from boiling water, was obtained in the form of white needles melting at  $143\text{--}144^\circ$  and formed a picrate melting at  $228\text{--}229^\circ$ . The melting points of the base and the picrate prove that the reduction of  $\alpha$ -nitromethylaceto- $\beta$ -naphthalide gives rise to the same *N*-methylamidine as that obtained by the direct methylation of Prager's ethenyldiaminonaphthalene (Otto Fischer, *Ber.*, 1901, 34, 935; Meldola, Eyre, and Lane, *Trans.*, 1903, 83, 1197). This *N*-alkylamidine is thus shown to be a  $\beta$ -NH-derivative and the corresponding amidine to be the  $\beta$ -NH-modification.

Reduction of the  $\alpha$ -nitromethylaceto- $\beta$ -naphthalide in alcoholic solution with zinc and acetic acid or with iron and hydrochloric acid results in the same  $\beta$ -*N*-methylamidine. The latter base was further characterised by conversion into the *platinichloride*, which was obtained in the form of microscopic, white needles melting with decomposition at about  $280^\circ$ .

0.1294 gave 0.0313 Pt.  $\text{Pt} = 24.18$ .

$(\text{C}_{13}\text{H}_{12}\text{N}_2)_2\text{H}_2\text{PtCl}_6$  requires  $\text{Pt} = 24.29$  per cent.

The *hydrochloride*,  $\text{C}_{13}\text{H}_{12}\text{N}_2\text{HCl}$ , separates in the form of white needles on adding excess of hydrochloric acid to a solution of the base in dilute acid; it melts when dry at  $272\text{--}273^\circ$  with previous softening.

The *chromate* is precipitated in the form of ochreous needles on adding a solution of potassium chromate to a solution of the acetate of the base; the dry salt decomposes on heating at  $188\text{--}194^\circ$ .

1-Nitroethyl- $\beta$ -naphthylamine,  $\text{C}_{10}\text{H}_6\text{NO}_2\text{NH}\cdot\text{C}_2\text{H}_5^{(2)}$ , was prepared in precisely the same way as the corresponding methyl derivative by heating  $\alpha$ -nitro- $\beta$ -naphthyl ethyl ether with an alcoholic solution of ethylamine. After crystallisation from glacial acetic acid and finally from alcohol, the pure compound was obtained in the form of bright orange-red prisms melting at  $100\text{--}101^\circ$ .

The *nitrosoamine*, prepared in the same way as the methylnitrosoamine, crystallises from alcohol in silvery scales melting at  $90^\circ$ .

0.1750 gave 25.1 c.c. moist nitrogen at  $14.7^\circ$  and 775 mm.  $\text{N} = 17.13$ .

$\text{C}_{12}\text{H}_{11}\text{O}_3\text{N}_3$  requires  $\text{N} = 17.17$  per cent.

This nitroethylnaphthylamine was acetylated in the same way as the corresponding methyl derivative, and the nitroethylacetonephthalide, after being washed free from acetic acid and sodium acetate, was reduced in alcoholic solution by tin and hydrochloric acid in the usual

way. After removal of the alcohol by distillation and of the tin as sulphide, the base was isolated as before and purified by solution in dilute oxalic acid and precipitation by alkali. The resinous base was characterised by conversion into the picrate, which proved to be identical with the picrate of the base obtained by the direct ethylation of Prager's amidine (Trans., 1903, 83, 1197). The melting point was  $248^{\circ}$ , and the following results were obtained on analysis:

0.1369 gave 18.8 c.c. moist nitrogen at  $15^{\circ}$  and 750 mm.  $N = 15.85$ .

$C_{14}H_{14}N_2 \cdot C_6H_2(NO_2)_3 \cdot OH$  requires  $N = 15.97$  per cent.

The same *N*-ethylamidine was obtained by first reducing the nitro-ethylnaphthylamine by zinc dust in acetic acid solution, and then converting it into the anhydro-base by prolonged boiling with excess of acetic acid and a little acetic anhydride.

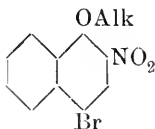
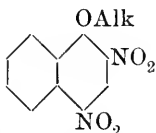
#### *Synthesis of $\alpha$ -N-Ethylamidines.*

The preparation of naphthalene derivatives containing an  $\alpha$ -*N*-alkyl substituent has presented remarkable difficulties, and much time was expended in preliminary experiments before any positive result was obtained. The evidence derived from the study of the  $\beta$ -*N*-alkylamidines, as above described, proved conclusively that Prager's ethenyldiaminonaphthalene and Markfeldt's ethenyltriaminonaphthalene were  $\beta$ -NH-amidines.

From this it follows indirectly, and on the supposition that structural isomerism is the cause of the difference between the two sets of bases, that our corresponding compounds were  $\alpha$ -NH-amidines.

The direct proof of this proposition therefore became absolutely essential in order to complete the evidence. This proof, which is given below, therefore carries with it the establishment of the fact that the isomerism under investigation is a case of ordinary structural isomerism brought about in a novel and unexpected way.

At the outset of this part of the work we encountered the same difficulty as that which has already been referred to in connection with the  $\beta$ -*N*-alkyl derivatives, namely, the impossibility of preparing compounds of the required type from ethyl- $\alpha$ -naphthylamine. A supply of the hydrochloride of the latter was kindly placed at our disposal by Messrs. Leopold Cassella & Co., of Frankfort. With this base, a number of experiments were tried, the results of which will be made known in a future communication, since they proved to be inconclusive so far as concerned the isomerism of the *N*-alkylamidines. The successful solution of the problem has depended ultimately on the discovery that compounds of the type



exchange their alkoxy-group for the alkylamino-group with extreme, and in fact with surprising, readiness, the substitution taking place even at the ordinary temperature. This reaction will appear the more remarkable when it is stated that the unalkylated compounds, namely, dinitro- $\alpha$ -naphthol and bromonitro- $\alpha$ -naphthol, can be heated with ethylamine solution to high temperatures without undergoing conversion into the corresponding ethyl- $\alpha$ -naphthylamine derivatives; at low temperatures no change occurs, and at high temperatures the products are resinified. The dinitro-derivative could not be made to yield the *N*-alkylamidine for reasons stated in the sequel. The experiments with the bromonitro-derivative are described below:—

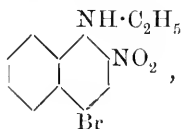
Bromonitroaceto- $\alpha$ -naphthalide was converted into 4-bromo-2-nitro- $\alpha$ -naphthol by hydrolysis (Biedermann and Remmers, *Ber.*, 1874, '7, 538; see also *Trans.*, 1892, 61, 765, footnote), and the bromonitro- $\alpha$ -naphthol into the silver salt by slightly warming the former with enough alcohol to form a thin paste, and adding to it the calculated quantity of silver oxide. The silver salt was then ethylated by adding the calculated quantity of ethyl iodide and boiling until the red colour of the silver salt had disappeared. By this process—and it was not found possible to improve it—about 30 per cent. of the bromonitronaphthol is ethylated, the unchanged compound being separated from the ether, after distilling off the excess of alcohol, by extraction with very dilute caustic soda solution and filtration. This 4-bromo-2-nitro- $\alpha$ -naphthyl ethyl ether does not appear to have been described before. It crystallises from alcohol in straw-coloured needles melting sharply at 80°.

0.2572 gave 0.1622 AgBr. Br = 26.84.

$C_{12}H_{10}O_3NBr$  requires Br = 27.0 per cent.

When a hot alcoholic solution of the ether is mixed with an alcoholic solution containing a slight excess of ethylamine, a red colour immediately appears, and on cooling red crystals of bromonitroethyl- $\alpha$ -naphthylamine separate out. The same change takes place, only more slowly, at the ordinary temperature.

4-Bromo-2-nitroethyl- $\alpha$ -naphthylamine,



when allowed to crystallise slowly from alcohol, forms long, flat needles of a bright orange-red colour. If, by sudden cooling of the hot solution, it is made to crystallise rapidly, it separates in the form of bright scarlet, silky, filamentous needles. Analysis showed that the compound dried in air contained alcohol of crystallisation :

0.1002 gave 7.0 c.c. moist nitrogen at  $17.7^{\circ}$  and 767.3 mm.  $N = 8.15$ .

$C_{12}H_{11}O_2N_2Br \cdot C_2H_6O$  requires  $N = 8.23$  per cent.

A specimen dried in the water-oven gave the following results :

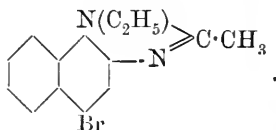
0.1271 gave 10.25 c.c. moist nitrogen at  $16.6^{\circ}$  and 762.5 mm.  $N = 9.40$ .

0.0918 „ 7.45 c.c. „ „ „  $16.1^{\circ}$  „ 767.5 mm.  $N = 9.54$ .

$C_{12}H_{11}O_2N_2Br$  requires  $N = 9.51$  per cent.

The acetylation of the bromonitro-compound could not be effected by boiling with acetic anhydride and anhydrous sodium acetate under ordinary atmospheric pressure. The acetyl derivative was, however, obtained by heating the compound with excess of acetic anhydride in a sealed tube at  $160-170^{\circ}$  for 3—4 hours. The product was resinous and no attempt was made to isolate it, but it was dissolved in alcohol and reduced in the usual way by boiling the solution with tin and hydrochloric acid. After distilling off the alcohol, the hydrochloride of the bromo-*N*-ethylamidine separated out, this salt being but very slightly soluble in the presence of excess of hydrochloric acid. The hydrochloride was basified by sodium hydroxide in alcohol and the solution boiled for 24 hours with excess of sodium amalgam. A qualitative and quantitative examination of the product showed that the bromine had not been removed even after this prolonged treatment with sodium amalgam.

The bromo-*N*-ethylamidine must, from its mode of formation, have the formula



The base is slightly soluble in boiling water and dissolves very readily in alcohol. From the latter solvent, when dilute, it crystallises in white, silky needles melting with previous softening at about  $110^{\circ}$ . All the salts have a great tendency to gelatinise when water is used as a solvent. The *picrate* forms yellow needles melting at  $265-266^{\circ}$ . We propose to characterise this base more fully when a further supply has been prepared. The property of immediate importance to the present research is that it can be debrominated by boiling the alcoholic solution with zinc dust and a little sodium hydroxide and excess of

ammonia for 12 hours. The product, after isolation, was proved qualitatively to be free from bromine and by means of its picrate (m. p. 234—235°) identified as the *N*-ethylamidine first obtained by the direct ethylation of the ethenyldiaminonaphthalene obtained from our (M. and S.) ethenyltriaminonaphthalene (Trans., 1903, 83, 1190, 1194). The  $\alpha$ -NH-constitution of the amidines of this series is thus proved by direct synthesis.

In concluding this paper, we desire to acknowledge the assistance which we received at the beginning of the Session 1903—1904 from Mr. R. W. L. Clarke.

FINSBURY TECHNICAL COLLEGE.

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CLXI.—*The Spectrum generally attributed to "Chlorophyll" and its Relation to the Spectrum of Living Green Tissues.*

By WALTER NOEL HARTLEY.

IN the Transactions of the Chemical Society for 1891, I pointed out that it had long been known that leaf-green is composed of at least two colouring matters, called blue and yellow chlorophylls respectively, the optical properties of which had been studied independently by Stokes and by Sorby. It was found desirable to adhere to their nomenclature rather than to adopt that of other investigators: firstly, because the principal observations in my paper were made on living tissues and were mainly spectroscopic; secondly, because the substances separated from leaves, whether dried at 100° in air or even *in vacuo* at normal temperatures, were shown by their spectra not to be the same as those contained in living tissues, the observed differences being in the green substance; and, thirdly, because such names as chlorophyll cyanophyll, phyllocyanin, chrysophyll, xanthophyll, and phylloxanthin could not be properly applied to substances which had not been isolated, particularly in those cases where the method of examination was entirely spectroscopic or where the substances were separated merely as solutions in different liquids. It was found that even apparently inert solvents such as ether, chloroform, and turpentine caused changes in the "blue chlorophyll" spectrum, resembling those which are caused by the action of acids. Experience in the extraction of colouring matters from the green leaves of plants showed

that, as far as possible, no water should be used, and that the operation should be conducted in darkness or in a subdued light, with as little exposure to air as possible. Light and air caused oxidation of the formaldehyde always present in the green extracts of leaves, and the acid formed in consequence caused changes in the colouring matters. Besides, the action of light alone was observed to bring about chemical changes in solutions of the separated colouring matters, and also in the chlorophylls contained in living tissues. One of the principal objects of the investigation was to ascertain the relationship of the absorption spectrum in the visible region to that in the ultra-violet, and also to examine separately the bluish-green colouring matter and those which are yellow. The result of numerous observations was that "no living green tissue of any kind was found to be capable of transmitting the ultra-violet rays."

C. A. Schunck (*Proc. Roy. Soc.*, 1899, 65, 177), quoting Sorby, states that the chlorophyll of the higher plants is separable into two colouring matters which he terms "blue chlorophyll" and "yellow chlorophyll," the former being the chief constituent, and that E. Schunck extracted sparkling red crystals which he considered to be identical with Bougarel's erythrophyll and Hartsen's chrysophyll. He next proceeds to say: "I will now give the results of the experiments I have made in the endeavour to separate these yellow colouring matters from the accompanying chlorophyll, dealing more especially with their spectroscopic relations as compared to those of chlorophyll in the violet and ultra-violet region of the spectrum investigated by the aid of photography. A means which, with the exception of Tschirch, former observers have not applied."

It is obvious that this statement is incorrect, for the following reasons. The paper entitled "The Spectra of Blue and Yellow Chlorophyll, with some Observations on Leaf-green," which was published eight years previously (*Trans.*, 1891, 59, 106), and which had occupied me for a period of more than five years, contained the following four series of observations:—

(a) The spectra of the chlorophyll contained in living tissues; (b) the spectrum of chlorophyll as seen in dried leaves; (c) a mode of extracting leaf-green unchanged, and separating the blue from the yellow chlorophyll; and (d) measurements of the spectra of the chlorophylls.

These spectra were measured by the eye in the red and up to the blue, and by photography in the blue, violet, and ultra-violet, with a quartz spectrograph in the manner continuously employed by me since 1880. The relationship of the spectra of the visible region to that in the ultra-violet both of the "blue chlorophyll" and of the "yellow chlorophyll" was elucidated, and diagrams were published

(*loc. cit.*, p. 121), showing, by curves drawn in the manner previously described, the relationship of the absorption of the "blue chlorophyll" in both the visible and ultra-violet regions to that of the yellow chlorophylls (or xanthophylls) in the substance contained in plant tissues which I termed "leaf-green."

The following points were claimed as new matter in that paper:—an examination of the views entertained by Pringsheim ("Researches on Chlorophyll," *Quart. Journ. Micros. Soc.*, 1882, 22, N.S., 113—135) as to the function of chlorophyll, with a demonstration that Pringsheim's explanation was inadequate, inasmuch as chlorophyll appeared to act as a ray filter rather than as a screen, and, above all, also as an absorbent of radiant energy.

This view was considered to have been established by the experiments of Paul Bert (*Compt. rend.*, 1878, 87, 695), Lommel (*Ann. Phys. Chem.*, 1871, 143, 568), Timiriazeff (*Compt. rend.*, 1885, 100, 851), Reinke (*Bot. Zeit.*, 1885), Regnard (*Compt. rend.*, 1885, 101, 1293), and Bonnet and Mangin (*Compt. rend.*, 1886, 102, 123). It was confirmed by showing: firstly, that as long as any chlorophyll is present in a leaf to give it the faintest colour, the violet and ultra-violet rays are absorbed; secondly, by reference to Chastaing's experiments, which showed the necessity to the plant of powerful absorption of the rays with great chemical activity, with complete transmission of the green and yellow; thirdly, by explaining the nature of the most probable of the chemical actions taking place within the plant cell, so as to show how necessary it is for the substances formed by the action of the green and yellow rays to be screened from those rays which cause oxidation, namely, the red. The very alterable character of chlorophyll in the living tissue is a function of its great photochemical activity.

My view was, and is still, that by whatever name one may call it, the active substance or group of substances in the living leaf shows a powerful absorption band in the red, but none appreciable in the green, and the spectrum ends in the bluish-green. Even while under observation with a powerful beam of light, bands of absorption may appear in the yellow and green by reason of abnormal chemical action, such as oxidation.

It would, however, perhaps be better to quote measurements made by me in 1884, when observing the spectrum transmitted by fronds of a green sea-weed in the living state, and afterwards when the weed had been dried and extracted with alcohol ("On Chlorophyll from the Deep Sea," *Proc. Roy. Soc. Edin.*, 1884—1885, 13, pp. 130—136). According to Sorby, green sea-weed contains only "blue chlorophyll," and no yellow or red colouring matters.

*The Absorption Spectrum of Chlorophyll as seen in the Fronds of Living Sea-weed.\**

Description of the spectrum.	$\lambda$
Termination in the red.....	7194
<b>Absorption band in the red .....</b>	<b>6820 to 6410</b>
Termination in the blue .....	4975

A second series of measurements gave the band in the red from  $\lambda$  6812 to 6377, but no band in the orange or green.

*The Absorption Spectrum of Chlorophyll extracted from the Dried Sea-weed by Alcohol.*

Description of the spectrum.	$\lambda$
Termination of spectrum in the red .....	7194
<b>Absorption band in the red .....</b>	<b>6779 to 6343</b>
Feeble absorption band in the orange.....	6131 to 6008
Feeble absorption band in the green .....	5702 to 5333

"The bands in the orange and green were much weaker in the colouring matter extracted from sea-weed than they usually appear to be when an alcoholic extract of leaves is examined, as they are caused in the latter case by substances of the xanthophyll group (Sorby, *Proc. Roy. Soc.*, 1873, 21, 442—483) and their alteration products."

Marchlewski and C. A. Schunck ("Notes on the Chemistry of Chlorophyll," *Trans.*, 1900, 77, 1080—1904) state that "as regards the chemical criterion of unaltered chlorophyll, it must be admitted that a product deserves the name of 'chlorophyll' only if it yields under the influence of acids phylloxanthin and phyllocyanin, or at least the latter, by the prolonged action of the acid." The precise mode of preparing cold alcoholic extracts of leaf-green was described very fully in my paper, and the nature of the spectra transmitted by different thicknesses of solution and at different dilutions were described also when photographed with a quartz spectrograph through very dilute solutions. There were at least eight of these spectra of which measurements were made and a diagram drawn. A careful description was given of the spectrum observed in living green tissues, such as leaves or fronds, when one, two, three, and four thicknesses were examined, and these were compared with those of solutions. Marchlewski and Schunck believe that some of these observations are erroneous, and state that the alcoholic leaf-green solution prepared in the manner described by me showed spectra which did not differ in any way

\* Possibly *Ulva latissima*.

from the one considered by them as the normal chlorophyll spectrum (except as regards a fourth band), but they "differ radically from the spectrum of Hartley's blue chlorophyll." My method for precipitating the "blue chlorophyll" from the cold alcoholic extract of ivy leaves consisted, shortly, in cautiously adding successive portions of a warm saturated solution of barium hydroxide to the alcohol and stirring it until most, if not all, of the green colouring matter was precipitated. The object of the barium hydroxide was to neutralise any acid in the solution, or any which might be formed subsequently by the oxidation of the formaldehyde which it contains.

The choice of barium hydroxide as an alkaline precipitant was determined by its solubility being greater than that of lime both in water and in alcohol, and consequently a minimum amount only of water is necessary for the solution which is added to the strong alcohol, so that it does not undergo great dilution. Another advantage was the facility with which it would saponify oily and resinous matters in which chlorophyll dissolves most easily; and a further consideration was the possibility of removing the barium hydroxide from the chlorophyll by the action of such a substance as would not cause any alteration in its spectrum.

The use of aqueous acid solutions is not admissible. It was believed that barium hydroxide would not combine with the green matter to form such a compound as Guignet's alkali chlorophyll or the zinc compound referred to by E. Schunck (*Proc. Roy. Soc.*, 1886, 39, 348—361), for, when the precipitated chlorophyll was washed on the filter but not dried, it dissolved readily in benzene. It is scarcely probable that it would do so if it were a barium compound.

Marchlewski and Schunck state that boric acid in the form of a mixture with glycerol and alcohol was employed for the separation of the chlorophyll from the "baryta compound," but this is not quite correct. The solution was prepared in the following manner:—Anhydrous glycerol was heated to about 150° and crystallised boric acid added in successive small quantities until the strong syrupy solution approached the point of saturation, and water was freely given off. This syrupy boroglyceride was largely diluted with absolute alcohol, and the dried barium compound was decomposed with it. It is stated by Marchlewski and Schunck that the ethereal solution of chlorophyll separated from the barium compound prepared by them exhibited very marked differences when compared with ordinary chlorophyll solutions, from which they concluded that the barium hydroxide used for its isolation had undoubtedly effected some chemical change in the colouring matter present in the original green leaf extracts. The differences they state were of two kinds: firstly, as to the bands observed in the spectrum; secondly, as to the colour obtained by Fremy's phyllocyanin

reaction with hydrochloric acid and ether. It may be as well to state here that, operating generally on ivy leaves, the processes of extraction and precipitation were performed many times, and at least ten or twelve specimens of the barium hydroxide precipitate were prepared in the course of five or six years. At least three different quantities of the yellow colouring matters were also prepared, being precipitated by barium hydroxide in large excess, whereas Schunck and Marchlewski say they could not obtain these substances by this process. In the summer of 1901, Mr. D. S. Jardin, a student in the Royal College of Science, Dublin, prepared two solutions of "blue chlorophyll," one from the cold alcoholic extract of ivy leaves and the other from the barium hydroxide precipitate. With both of these he obtained the phyllocyanin reaction and compared the two; moreover, he measured the position of the bands in each solution. The notes of his experiments were made without any knowledge of Marchlewski and Schunck's communication or reference to their results.

In order to test once more whether the "blue chlorophyll," when precipitated by the barium hydroxide solution, would yield the phyllocyanin reaction, some leaves of Virginia creeper were gathered and cut away from the stalk and midrib. They were then minced and macerated in cold absolute alcohol contained in closed vessels completely filled and kept in a photographic dark room. The liquid was very rapidly passed through a filter, and it was then seen that the shredded leaves had lost nearly all their green colouring matter. Two portions of the solution, each measuring 100 c.c., were treated differently.

*Portion A* was precipitated by adding warm barium hydroxide solution, made by dissolving the crystallised substance in boiling distilled water, and allowing it to cool under a bell jar in order to protect it from carbon dioxide. The liquid, after precipitation by the barium hydroxide solution, was rapidly filtered and the yellow filtrate put aside; the green precipitate was washed on the filter with absolute alcohol, then with water, again once or twice with alcohol, and, after drying, with hot chloroform. Neither the water nor the chloroform extracted any notable proportion of colouring matter, and in this respect the behaviour of the solution was different from that extracted from ivy leaves. The substance on the filter paper was then dried *in vacuo*.

*Portion B.*—This solution was distilled on the water-bath in a flask protected from light until 93 c.c. out of 95 c.c. of the alcohol had been separated. The residue was mixed with an equal volume of water, whereby the "blue chlorophyll" was separated as an emulsion along with the other matters, and it was then shaken with benzene, which dissolved the colouring matter, forming a green solution. This solution was

reduced in volume by evaporation to about one-fourth, and subsequently mixed with strong hydrochloric acid.

*Treatment of Portion A, Barium Hydroxide Precipitate.*—The barium hydroxide chlorophyll precipitate was dissolved in a mixture of 1 c.c. of water with 1 c.c. of fuming hydrochloric acid, and as the substance was not freely soluble in this mixture a further addition of 2 c.c. of hydrochloric acid was made; 5 c.c. of ether were then added and the mixture shaken in a stoppered cylinder 10 mm. in diameter. The aqueous solution and the ethereal layer were allowed to separate without any turbidity, when barely a trace of colour was seen in the ether, which had a pale madder-brown tint.

*Portion B. Benzene Extract from Cold Alcoholic Solution.*—The same operation was carried out with the concentrated benzene solution; a similar volume in a similar stoppered cylinder when treated with hydrochloric acid and ether gave to the solvent a yellowish-brown and finally a yellow colour.

The hydrochloric acid both in portion *A* and portion *B* was blue with a tinge of green—the colour in each cylinder being precisely the same in tint, but in *B* it was apparently very slightly darker.

The spectra of the two solutions were examined and carefully measured. With a direct-vision spectroscope and without measuring, the spectra of the two liquids looked precisely alike. The measurements were made with a spectroscope of A. Hilger's make, fitted with a scale of wave-lengths, the *D* lines being well separated.

The spectra were examined and measured both by the Welsbach light and by sunlight.

The following are the measurements of the spectra of these solutions contained in cylinders of the same diameter which, acting as cylindrical lenses in front of the slit, focussed the transmitted rays upon it. Two series of measurements were made, one by the Welsbach light, the other by sunlight reflected from a heliostat.

*A*<sup>1</sup>.—Chlorophyll separated from the barium hydroxide precipitate and submitted to the phyllocyanin reaction. Welsbach light.

*A*<sup>2</sup>.—The same, examined by sunlight with a narrower slit than *A*<sup>1</sup>, giving a beautifully sharp definition of the solar lines.

*B*<sup>1</sup>.—Chlorophyll separated from a cold alcoholic solution, precipitated by water and agitated with benzene. The benzene solution was separated, concentrated, and agitated with hydrochloric acid precisely in the same manner as *A*<sup>1</sup>.

*B*<sup>2</sup>.—The same as in *A*<sup>2</sup> when examined by sunlight.

	$A^1.$ $\lambda$	$A^2.$ $\lambda$	$B^1.$ $\lambda$	$B^2.$ $\lambda$
Termination of the spectrum in the red .....	740	750	720	750
Powerful absorption band in the red, edges very distinct .....	700 to 650	685 to 655	685 to 645	680 to 645
As a mere shade, diffuse, not distinct. Very difficult to measure. Indication of a band .....	585—575	585—575	587—575	590—580
Extremely feeble shade. Very difficult to measure .....	540—525	Not visible	540—530	Not visible
Termination in the blue .....	451	451	451	451

Readings on the scale made with a narrow slit and sunlight gave the following wave-lengths for the solar lines, *A* 750, *B* 687, *C* 656, and *D* 589, the last being the mean number for  $D^1$  and  $D^2$ .

It was decided to concentrate the two solutions by dissolving the colouring matter in carefully purified chloroform. This was done in both cases, and the examination of the two solutions was made with sunlight.

	$A.$ $\lambda$	$B.$ $\lambda$
Termination of the spectrum in the red.....	750	750
Absorption band in the red ..	700—647	690—640
Absorption band in the yellow .....	585—575	590—575
A shade in the green, very faint .....	Not visible	547—537
End of spectrum in the blue .....	451	451—455

After the treatment with chloroform, *A* gave the purer blue colour. From *B*, some brown substance separated from the blue solution. For comparison with the measurements given above, a green leaf was removed from a fig-tree at the moment of measuring and examined.

	$\lambda$
Termination of the spectrum in the red .....	730
Absorption band in the red.....	690—650
No band in the green or yellow. End of spectrum in the blue .....	451

*Solution B.*—A very slightly coloured solution was examined by sunlight as before.

	$\lambda$	$\lambda$
Termination of the spectrum in the red .....	715	With less light 760
Very distinct absorption band in the red.	670—657	

*Solution B.*—After treatment with hydrochloric acid, the yellow ethereal extract floating on the blue aqueous solution was examined.

	$\lambda$	
Termination of the spectrum in the red .....	720	
A well - marked, <b>very strong band</b> in the red .....	675—645 ←	This is the first band of the blue solution obtained by the phylloeyanin reaction, and it indicates an incomplete separation of that substance from the yellow colouring matters.
A faint band, or rather a shade .....	605—595	
A very faint shade.....	565—555	
A band very weak, but distinct.....	540—530 ←	This band belongs, evidently, to the yellow chlorophyll. It appeared in the blue solution produced when preparation <i>B</i> was submitted to the phylloeyanin reaction.
End of spectrum in the blue .....	440	

In a foot-note to their paper, Marchlewski and Schunck confirm my observations published in 1891 regarding the spectrum transmitted by the living leaf.

The statements made in my paper have, I think, been justified by these measurements, namely, that the colouring matters from ivy leaves were extracted apparently in an unchanged condition, at least so far as spectroscopic observations made at different stages of the process can afford evidence of a change in composition. It should be understood where the chlorophyll was described as unchanged it is implied that such changes in the spectra of the substance as are caused by (*a*) drying, (*b*) by acids, (*c*) by the action of light, or (*d*) by oxidation, were not detected in the solutions.

Étard has shown that a knowledge of chlorophyll can be extended only by examining large quantities of a chlorophyll of a definite composition (*Compt. rend.*, 1896, 123, 824). Chlorophylls from different species of plants are different;  $\alpha$ -medicago-chlorophyll,  $C_{28}H_{45}O_4N$ , and  $\alpha$ -borago-chlorophyll,  $C_{34}H_{53}O_{12}N$ , the former from lucerne and the latter from borage, have been examined in the same solvents and in the same degrees of concentration, namely, 1/400th, 1/1000th, and 1/10,000th; mere variations in the thickness of the layer of solution, or of the degree of concentration of the solution in the same thickness, are sufficient to cause one chlorophyll to be mistaken for another.

The spectra of the two substances are different in the number and position of the bands: the former compound shows three bands between the general absorption at the red end and that at the violet; the latter shows five bands. If the formulæ assigned to the two substances by Étard be examined, it will be seen that the difference between them is  $C_6H_8O_8$ , and taking into account that formaldehyde is constantly present in the green parts of plants, that four molecules of it contain  $C_4H_8O_4$ , that it combines with a great variety of organic substances, and, furthermore, that chlorophyll, that is to say,

the green coloring matter of leaves, absorbs carbon dioxide forming an unstable compound with it (Hansen, *Abstr.*, 1888, 54, 867; and E. Schunck, *Ann. Botany*, 1889—1890, 3, 65—120), two molecules of carbon dioxide, if added to the four of formaldehyde, would yield  $C_6H_8O_8$ , this being the difference shown above between the medicago- and borago-chlorophylls.

The view put forward in my paper (*Trans.*, 1891, 59, 124) as being more probable on purely chemical grounds was that the unstable compound of chlorophyll with carbon dioxide is entirely altered firstly by the elimination of oxygen, and secondly by the elimination of water, so that there are successively formed compounds of chlorophyll (1) with carbon dioxide, (2) with formaldehyde, (3) with glucose, and, finally, completely formed starch is eliminated from the molecule.

Lastly, I should like to remark that C. A. Schunck's observations on the yellow substances present in, and separated from, green leaves show more bands than I observed (*Proc. Roy. Soc.*, 1899, 65, 177, and 1901, 68, 475). This is easily accounted for, as some of the bands are extremely feeble, and the solar lines which he shows on his beautiful photographs about *F* and *G* are much broader than in my spectra, which indicates either that the slit he used was wider, or at that point that the spectrum was not in good focus. Hence very weak bands appear in his spectra but not in mine. My measurements were the following :

*The Alcoholic Solution of the Yellow Chlorophyll (or Xanthophyll, according to Sorby) was examined both by the Eye and by Photography.*

Thickness of solution.	Eye Observations.	$\lambda$
mm.		
15	{ Termination of the spectrum in the red at .....	719
	{ The centre of a very feeble absorption band overlying	
	{ C, difficult to measure, the edges being too diffuse ...	660
5	{ Spectrum ends in the red at .....	719
	{ Spectrum ends in the blue at .....	490

*Photographed Spectra.*

mm.		$\lambda$	$\lambda$
5, 4, 3	Ill-defined <b>absorption band</b> , strong .....	518 to	467
	{ Spectrum begins (between <i>F</i> and <i>G</i> ) at .....	467	
2	{ Continuous feebly to .....	440	
	{ <b>Absorption band</b> , strong .....	440 to	407
1	Continuous spectrum from near <i>F</i> .....	480	
	to .....	256	

*The Solution was diluted to Five Times its Volume.*

mm.		$\lambda$
5, 4, 3	A continuous weak spectrum to .....	256
2	A continuous weak spectrum to .....	231

*Another Preparation in a more Concentrated Alcoholic Solution.*

mm.		$\lambda$
20	{ Spectrum begins in the red at.....	719
	{ Weak absorption band .....	670 to 658
	{ Spectrum ends in the green at.....	502

I also separated another yellow colouring matter which showed no absorption band, but it greatly enfeebled the spectrum in the ultra-violet, even in very thin layers.

ROYAL COLLEGE OF SCIENCE,  
STEPHEN'S GREEN,  
DUBLIN.

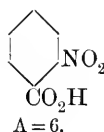
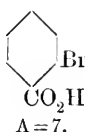
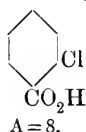
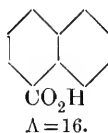
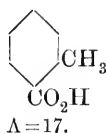
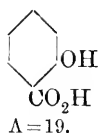
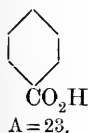
CLXII.—*Studies on Comparative Cryoscopy. Part II.*  
*The Aromatic Acids in Phenol Solution.*

By PHILIP WILFRED ROBERTSON, B.A.

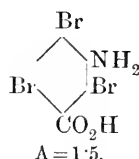
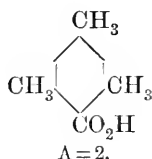
IN a previous communication (Trans., 1903, 83, 1426), an account was given of the results obtained from the cryoscopic examination of the phenolic solutions of the fatty acids and their derivatives. It was shown that substitution of the  $\alpha$ -hydrogen of an acid reduced the "rate" of association, and that the values of this constant bore an intimate relationship to the velocity of esterification.

On extending this research to the aromatic acids, it has been again found that those acids which are most difficult to esterify show the smallest "rate" of association. As a general rule, it may be stated that substitution in the ortho-position with respect to carboxyl reduces the "rate" of association. The lighter groups (OH, CH<sub>3</sub>) exert only a slight influence, but there is a marked diminution in the case of the heavier groups (Cl, Br, NO<sub>2</sub>).

These conclusions may be illustrated by means of the following compounds:



In the case of the diortho-substituted acids, however, there is practically no association, and in these compounds the substituent groups or atoms have the same influence, whether they are heavy or light. Thus:



In this connection it is interesting to note that, whereas the rate of esterification of the ortho-substituted benzoic acids is dependent on the weight of the substituent group, V. Meyer has shown that, in general, diortho-substituted acids yield no trace of ester when treated in the cold with hydrochloric acid and methyl alcohol. With such a clear connection between the esterification and association, it can hardly be doubted that the former process is preceded by the formation of an unstable additive product between the acid and the alcohol.

The method of experiment and the calculation of results have already been described (*loc. cit.*). Unfortunately the number of compounds which could be examined was limited owing to the fact that many of the aromatic acids are only sparingly soluble in phenol.

The experimental results are collected in Table I. As in the previous communication,  $A$  denotes the "rate" of association and  $\Delta_1$  represents the molecular depression for a fall of  $1^\circ$ .

TABLE I.

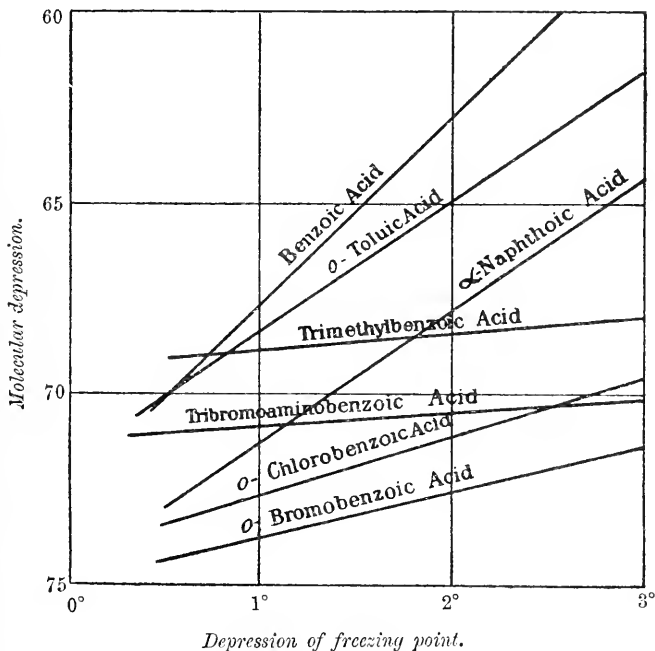
Acid.	$A$ .	$\Delta_1$ .	Acid.	$A$ .	$\Delta_1$ .
1. Benzoic .....	23	70	10. <i>o</i> -Chlorobenzoic.....	8	73.5
2. <i>o</i> -Toluic .....	17	70	11. <i>o</i> -Bromobenzoic.....	7	74.5
3. <i>m</i> -Toluic .....	23	71.5	12. Tribromoaminobenzoic	1.5	71
4. <i>s</i> -Trimethylbenzoic .....	2	68	13. <i>o</i> -Nitrobenzoic .....	6	72
5. Mesitylenic .....	19	69	14. <i>m</i> -Nitrobenzoic .....	14	70
6. $\alpha$ -Naphthoic.....	16	73	15. <i>o</i> -Aminobenzoic .....	25	72.5
7. Salicylic .....	19	67	16. <i>p</i> -Aminobenzoic .....	34	73.5
8. <i>o</i> -Cresotic .....	18	72	17. <i>o</i> -Acetoxybenzoic .....	6	69
9. Anisic .....	19	72.5	18. <i>p</i> -Acetylaminobenzoic	25	74

The behaviour of the various acids is graphically represented in the accompanying figure (p. 1619).

*Benzoic Acid, its Methyl Derivatives, and Naphthoic Acid.*

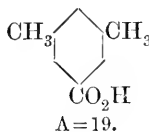
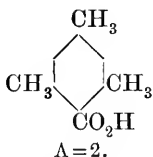
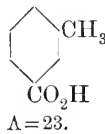
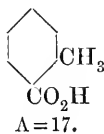
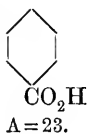
The value of  $A$  in the case of benzoic acid is 23. From the result obtained for *o*-toluic acid, it is seen that the introduction of methyl in

the ortho-position reduces the "rate" of association from 23 to 17. In the meta-position, however, the methyl group exerts no influence, as *m*-toluic acid associates as rapidly as benzoic acid itself. Two methyls in the ortho-position prevent association, as *s*-trimethylbenzoic acid is practically normal. But in the meta-position two of these



groups have no such influence, mesitylenic acid associating almost as rapidly as benzoic acid.

Thus



$\alpha$ -naphthoic acid behaves similarly to *o*-toluic acid.

*The Hydroxy-acids.*

Most of these acids were not sufficiently soluble to be examined. From the value for salicylic acid ( $A=19$ ), it is seen that the hydroxyl group in the ortho-position exerts almost the same influence as methyl. *o*-Cresotic acid (1:2:3) associates as rapidly as salicylic acid. As in the case of *m*-toluic acid, a methyl group in the meta-position does not affect the "rate" of association. The experimental number for anisic acid ( $A=19$ ) shows that a methoxyl group in the para-position causes a slight reduction in the "rate" of association.

*The Halogen and Nitroxyl Derivatives.*

The influence of the chloro-, bromo-, and nitro-groups in the ortho-position is almost identical, reducing the association of benzoic acid to one-third of its value. Diortho-substitution by bromine in the case of tribromoaminobenzoic acid practically prevents association.

In the meta-position also the nitro-group reduces the association considerably, whereas the methyl group in the same position exerts no influence.

*The Amino-acids.*

Whereas *o*-aminobenzoic acid associates somewhat more rapidly than benzoic acid, the increase in the case of the para-derivative becomes considerable. As formerly shown in the case of *isonitrosovaleric acid* (*loc. cit.*), the association is, in this instance, due to secondary influences. It is caused by the union of a carboxyl of one molecule with the amino-group of another. This was shown by the fact that when benzoic acid was added to a solution of phenol containing aniline, an abnormally low molecular depression was observed, indicating a probable union between the acid and the base. The following are the experimental data:

A solution of aniline in 9.85 grams of phenol causing a depression of 3°.			A solution of <i>m</i> -xylene in 9.3 grams of phenol causing a depression of 3°.		
Weight of benzoic acid added.	$\Delta t.$	Molecular depression.	Weight of benzoic acid added.	$\Delta t.$	Molecular depression.
0.1560	0.73°	56	0.1646	0.96°	65
0.2424	1.12	56	0.1040	0.57	61
0.1862	0.83	54	0.1514	0.80	59
0.1494	0.67	54			

In the presence of the *m*-xylene, which does not unite with benzoic acid to form a molecular complex, the depression is much greater and decreases rapidly.

That *p*-aminobenzoic acid associates more rapidly than the ortho-

derivative is to be expected from the well-known fact that amino-compounds with acid groups in the para-position are more basic than the isomeric compounds.

*Acids with Negative Rates of Association.*

The acetoxy- and acetylamino-groups are found to have a negative influence upon the "rates" of association, so that the apparent molecular weight of the compounds decreases with the concentration of the solution. Not only is this the case, but the effect of the group with the negative influence is disturbed by an associated group, and in the case of *p*-acetylaminobenzoic acid it appears to be intensified.

Thus :

Benzoic acid ( $A = 23$ ).

Acetanilide,  $A = -15$ .

Phenyl acetate,  $A = -7$ .

*p*-Acetylaminobenzoic acid,  $A = -25$ .    *o*-Acetoxibenzoic acid,  $A = -6$ .

*The Aromatic Acids in other Solvents.*

The only other cryoscopic investigation on the aromatic acids is that of Auwers and Orton (*Zeit. physikal. Chem.*, 1896, 21, 369). These observers used naphthalene as a solvent. It was shown that the meta-acids scarcely differed from benzoic acid, and that substitution in the ortho-position caused a very slight reduction in the amount of the association. From the few experiments which they could perform with the sparingly soluble diortho-acids, it appeared that the association was considerably reduced.

*The Solubility of the Aromatic Acids in Phenol.*

Just as the fatty dibasic acids proved to be sparingly soluble, so do phthalic and terephthalic acids dissolve with difficulty; the latter especially is extremely insoluble, its saturated solution causing a depression of only  $0.02^\circ$ . Thus terephthalic acid dissolves in phenol to the extent of 1 part in 2000.

The aromatic hydroxy-acids also are characterised by sparing solubility; as in the case of the fatty acids, a hydroxy-group was likewise found to diminish the solubility.

The amino-acids and their derivatives dissolve with comparative ease. The *o*- and *m*-nitrobenzoic acids are also readily soluble in phenol.

In Table II, the differences between the freezing points of phenol and its saturated solution are given for a number of slightly soluble acids. From these values are calculated the weights of substance dissolved by 100 grams of phenol.

TABLE II.

Acid.	Depression of freezing point of saturated solution.	Parts per 100.
$\alpha$ -Naphthoic .....	2.8°	6.5
$\beta$ -Naphthoic .....	1.8	4.1
Salicylic .....	2.9	6.3
<i>m</i> -Hydroxybenzoic .....	0.74	1.4
<i>p</i> -Hydroxybenzoic .....	0.40	0.76
$\alpha$ -Hydroxynaphthoic .....	0.45	1.1
$\beta$ -Hydroxynaphthoic .....	0.76	2.0
1 : 2 : 3-Cresotic .....	1.95	4.3
Anisic .....	1.9	4.2
Terephthalic .....	0.02	0.05
<i>p</i> -Bromobenzoic .....	0.23	0.64
<i>p</i> -Nitrobenzoic.....	0.56	1.3
<i>m</i> -Aminobenzoic .....	2.2	4.3
<i>p</i> -Acetylaminobenzoic.....	2.4	5.5

VICTORIA COLLEGE LABORATORY,  
WELLINGTON,  
NEW ZEALAND.

### CLXIII.—*The Influence of Substitution in the Nucleus on the Rate of Oxidation of the Side-chain. II. Oxidation of the Halogen Derivatives of Toluene.*

By JULIUS BEREND COHEN and JAMES MILLER.

OUR first paper on this subject contained an account of the action of dilute nitric acid on the mono- and di-chlorotoluenes (Trans., 1904, 85, 174).\*

We have now studied the behaviour of the isomeric chlorobromotoluenes and dibromotoluenes and the 2:6-chloroiodo-, bromoiodo-,

\* Our attention has been called to the fact that, in the brief reference which we made to previous investigations on this subject, we omitted—the oversight was quite unintentional—to mention the name of Professor Ira Remsen. The statement contained in Lellmann's *Organische Synthese*, and referred to by us, that “negative atomic groups in the ortho-position protect the alkyl group from the action of acid oxidising agents, whereas alkaline oxidising agents attack this group,” was the outcome of a series of investigations carried out by Remsen and his pupils from 1877 onwards, which appeared in the *American Chemical Journal*. The above statement, in the light of Prof. Remsen's subsequent work, requires modification. He finds that negative atomic groups in the ortho-position protect the alkyl group from the action of oxidising agents, but it is not true that alkaline oxidising agents attack this group, although there are some cases in which this last statement holds good.

and di-iodo-toluenes. The last three lose iodine readily on oxidation with dilute nitric acid, and the same is true of the monoiodo-compounds, although to a much smaller extent. In consequence of this decomposition, the study of the dihalogen compounds containing iodine was discontinued.

The following table contains a synopsis of the results with the three series of dihalogen compounds, the substances on the left being least, those on the right most rapidly oxidised. The bracket indicates an approximately equal rate of oxidation.

TABLE I.

Cl : Cl.....	3 : 5	2 : 5	2 : 6	2 : 3	2 : 4	3 : 4
Cl : Br ...	3 : 5	2 : 5	2 : 6	2 : 3	2 : 4	3 : 4
Br : Cl ...		2 : 5		2 : 3	2 : 4	3 : 4
Br : Br ...	3 : 5	2 : 3	2 : 5	2 : 6	2 : 4	3 : 4

The order of oxidation is the same in all three series with the exception of the 2 : 3-dibromotoluene, which follows the 3 : 5- instead of the 2 : 5- and 2 : 6-compounds, as in the other two series. This fact is of some importance and will be referred to again.

The experiments have been carried out in the apparatus previously described (*loc. cit.*) and with about the same quantity of materials. The amounts of unchanged substance and acid have been estimated in each case, but the results are calculated from the amount of acid as yielding on the whole the most trustworthy figures. From the acid, the corresponding amount of toluene derivative has been calculated and given in parts per hundred of substance taken.

The following table gives the figures for the chlorobromotoluenes :

TABLE II.

Cl : Br.	Per cent. oxidised.	Δ	Δ per cent. oxidised.	Cl : Br.	Per cent. oxidised.	Δ	Δ per cent. oxidised.
2 : 3	59.0	3.2	5	2 : 6	46.1	1.1	1.3
3 : 2	62.2			3 : 4	84.4		
2 : 4	74.6			4 : 3	83.5		
4 : 2	71.1	3.5	5	3 : 5	28.4		
2 : 5	45.4						
5 : 2	48.1						

A comparison of the pairs of compounds with reversed positions of the halogens indicates that the compound in which bromine occupies the meta-position is the less oxidised of the two. Thus, 2 : 3-, 2 : 5-,

and 4 : 3-chlorobromotoluenes are less oxidised than the complementary compounds of each pair. The same is true of bromine in the ortho-position, the 4 : 2-compound being less oxidised than the 2 : 4-compound. The influence of the meta-bromine is least in the 3 : 4-compounds. The following is a similar table containing the results of two experiments made with the dibromotoluenes.

TABLE III.

Br : Br.	Per cent. oxidised.		Br : Br.	Per cent oxidised.	
	I.	II.		I.	II.
2 : 3	22.7	17.6	2 : 6	26.5	25.7
2 : 4	50.0	53.3	3 : 4	49.8	51.7
2 : 5	23.3	21.7	3 : 5	13.6	14.6

Making allowance for the various sources of experimental error incidental to the process, the results are fairly concordant. These errors may arise from the method of analysis, which does not afford great precision; from a portion of partially oxidised material remaining as aldehyde with the unchanged substance; from differences in the surface of contact exposed to the action of the acid and from the different solubilities in nitric acid of the halogen compounds and their oxidation products. We have tried as far as possible to obviate the source of error due to surface of contact by carefully selecting tubes of the same diameter. In the experiments which we have now to record, where comparative determinations of three series of halogen compounds have been made, we have used in all cases tubes made from the same length of tubing, and therefore as nearly as possible identical in diameter and approximately so in length.

Supposing the bromine in the ortho- and meta-positions to retard oxidation more than the chlorine in those positions, the effect should become apparent when the isotopic\* dichloro-, chlorobromo-, and dibromo-toluenes are oxidised together.

The following table contains the results of such a series of determinations. The weights of the substances taken for a given quantity of acid were approximately in the proportion of their molecular weights. The results as a whole are not strictly comparable, as each horizontal series represents a separate experiment. On the other hand, as the temperature and time of heating were nearly the same (with the exception of the 2 : 6 series, where for some unexplained reason the temperature inside the air-bath rose 5° higher than that in the

\* We propose, in future, to employ the word "*isotopic*" (*ίσος*, equal; *τόπος*, place) in place of the rather awkward expression "similarly substituted."

jacket), the vertical columns should, and do, in fact, correspond closely with the previous tables.

TABLE IV.

	Per cent. oxidised.			
	Cl : Cl.	Cl : Br.	Br : Cl.	Br : Br.
2 : 3	33·2	34·4	35·7	22·8
2 : 4	45·8	42·2*	40·1	42·6
2 : 5	23·5	18·0	19·1*	18·3
2 : 6	38·3	28·5	—	33·7
3 : 4	52·0	54·2	53·9	37·5
3 : 5	11·0	10·3	—	7·6

To render the figures in the horizontal series strictly comparable, the differences should be estimated on the percentage of substance oxidised. The relation of the dichloro- to the dibromo-compounds will then appear as follows :

TABLE V.

	Per cent. oxidised.		$\Delta$	$\Delta$ per cent. oxidised.
	Cl : Cl.	Br : Br.		
2 : 3	33·2	22·8	9·4	28
2 : 4	45·8	42·6	3·2	7
2 : 5	23·5	18·3	5·2	22
2 : 6	38·3	33·7	4·6	12
3 : 4	52·0	37·5	14·5	28
3 : 5	11·0	7·6	3·4	31

It is clear from the table that the dibromotoluenes are in all cases less oxidised than the dichloro-compounds. This result naturally follows from the effect already noted in the case of the chlorobromotoluenes, where bromine in the meta- and ortho-positions was found to retard oxidation more than chlorine. It will be seen, moreover, that where bromine occupies the meta-position, the retarding action is much more pronounced than in the other cases. The 2 : 3-, 2 : 5-, 3 : 4-, and 3 : 5-compounds all contain meta-bromine. It is also evident that the bromine in the para-position has little effect on the rate of oxidation. For if we assume that the lowering of the rate of oxidation in the 2 : 6-dibromo-compound (12 per cent.) is approximately divided between the two bromine atoms, the result will be almost equivalent to the decrease in the 2 : 4-compound (7 per cent.), leaving only 1 per cent. due to the influence of the para-bromine.

\* Owing to insufficient material, this number is not determined directly from experiment, but is calculated from Table II, p. 1623.

These interesting and apparently simple relations which determine the rate of oxidation in the case of the dichloro- and dibromo-compounds seem to vanish when the chlorobromo-derivatives are considered. From analogy with the dichloro- and dibromo-toluenes, the chlorobromotoluenes should occupy a position midway between these two series. The anomalous behaviour of the latter and the complexity of the whole problem involved can only be understood by reference to the rate of oxidation of the monohalogen compounds. The following two typical results are selected from a number of determinations:

TABLE VI.

Name.	I.	II.
	30 mins. 140—148°.	60 mins: 130—135°.
<i>o</i> -Chlorotoluene .....	7.5	8.6
<i>m</i> -Chlorotoluene .....	5.2	7.4
<i>p</i> -Chlorotoluene .....	16.2	13.7
<i>o</i> -Bromotoluene .....	24.7	23.5
<i>m</i> -Bromotoluene .....	17.4	19.0
<i>p</i> -Bromotoluene .....	48.7	43.6
<i>o</i> -Iodotoluene .....	5.2	5.9
<i>m</i> -Iodotoluene .....	7.2	8.6
<i>p</i> -Iodotoluene .....	7.0	7.5

It is evident from these figures that the presence of a bromine atom in the nucleus produces more rapid oxidation of the side-chain than that of a chlorine or an iodine atom. Why is it, then, that two bromine atoms should have the very reverse effect as compared with two chlorine atoms? It is evident that two similar atoms in the nucleus affect one another in a very marked degree. If proof of this were wanting, we have only to consider the effect of two bromine atoms in juxtaposition, namely, in the 2:3- and 3:4-compounds in Table IV. The drop in the rate of oxidation as compared with the isotopic dihalogen compounds is very clearly indicated in this table. Now it is precisely in these two cases that the rate of oxidation of the chlorobromo-compounds is more rapid than in that of the dichloro-compounds. Only one conclusion seems admissible, namely, that dissimilar atoms interfere less with each other's action than similar atoms, and that in consequence this factor must be considered, along with the position of the atoms in the nucleus, in determining the rate of oxidation. These two factors might very well explain the apparent anomalies in the relative rates of oxidation of the isotopic dihalogen compounds. It is impossible, however, with the present data, so to distribute the effect as to be able to predict the precise result in any given case.

## EXPERIMENTAL.

The chlorobromotoluenes for these experiments were prepared as described by Cohen and Raper (this vol., p. 1262). The dibromotoluenes were obtained in a similar manner, the 2:3-, 2:4-, 2:5-, and 2:6-compounds from the corresponding nitrotoluidines, and the 3:4- and 3:5-isomerides from aceto-*p*-toluidide by bromination. The chloro- and iodo-toluenes and *p*-bromotoluene were obtained from the corresponding toluidines. *o*- and *m*-Bromotoluenes are best prepared from bromo-*m*- and bromo-*p*-acetotoluidides respectively by removing the amino-group. Although, as already stated, the 2:6-chloriodo-, bromiodo-, and di-iodo-toluenes decompose on oxidation with nitric acid liberating iodine, it was thought desirable to record briefly the properties of these new compounds and of such intermediate products as have not been previously described.

*2-Chloro-6-iodotoluene* was prepared from 2-chloro-6-aminotoluene by the usual method; it is a colourless liquid, boiling at 132—133°/25 mm. and having a sp. gr. 1·844 at 20°/20°.

0·2668 gave 0·4008 AgCl + AgI.

$C_7H_6ICl$  requires 0·3999 AgCl + AgI.

*2-Bromo-6-iodotoluene* was obtained from 2-bromo-6-aminotoluene. The base forms a benzoyl derivative (m. p. 176—177°) and an acetyl derivative (m. p. 154—155°). Bromiodotoluene is a colourless liquid (b. p. 135—140°/15 mm.; sp. gr. 2·044 at 20°/20°).

0·2106 gave 0·2977 AgBr + AgI.

$C_7H_6IBr$  requires 0·2998 AgBr + AgI.

*2:6-Di-iodotoluene*.—Nitroiodotoluene crystallises in yellow needles (m. p. 34—36°). The 2-iodo-6-aminotoluene is a liquid; its hydrochloride crystallises in plates with a satiny lustre.

The di-iodotoluene crystallises from alcohol in nearly colourless needles (m. p. 40—42°).

0·2058 gave 0·2814 AgI. I = 73·87.

$C_7H_6I_2$  requires I = 73·82 per cent.

The following tables contain experimental data to which reference has already been made. The strength and quantity of nitric acid used was that employed in the previous experiments with the dichlorotoluenes, namely, 6 c.c. of nitric acid (1 vol. of acid, sp. gr. 1·4, to 2 vols. of water).

*Oxidation of the Chlorobromotoluenes.*

## Series I.

Time, 1½ hours. Temperature, 139—147°.

Cl : Br.	Weight.	Acid.	Unchanged.	Total.	M. p. of acid.	Correct m. p.
2 : 3	0.994	0.672	0.363	1.035	154—158°	165°
3 : 2	1.019	0.726	0.374	1.100	125—136	143—144
2 : 4	0.998	0.853	0.228	1.081	161—163	166—167
4 : 2	0.993	0.809	0.265	1.074	150—152	154—155
2 : 5	0.989	0.515	0.523	1.038	146—151	155—156
5 : 2	1.029	0.568	0.510	1.078	119—126	148—149
2 : 6	1.000	0.529	0.521	1.050	119—133	143—144
3 : 4	1.003	0.970	0.133	1.103	208—210	218
4 : 3	0.990	0.947	0.132	1.079	208—210	214
3 : 5	0.989	0.322	0.659	1.011	186—187	189—190

*Oxidation of the Dibromotoluenes.*

## Series II.

Time, 1 hour, 40 minutes. Temperature, 130—140°.

Br : Br.	Weight taken.	Acid.	Unchanged.	Total.	M. p. of acid.	Correct m. p.
2 : 3	0.990	0.252	0.800	1.052	139—144°	149—150°
2 : 4	1.024	0.574	0.519	1.093	156—158	158—159
2 : 5	1.032	0.270	0.819	1.089	140—146	153—154
2 : 6	1.011	0.300	0.777	1.077	93—117	146—147
3 : 4	1.012	0.565	0.514	1.079	225—226	229—230
3 : 5	0.990	0.151	0.838	0.989	210—212	213—214

*Oxidation of the Dibromotoluenes.*

## Series III.

Time, 1 hour, 45 minutes. Temperature, 130—140.5°.

Br : Br.	Weight taken.	Acid.	Unchanged.	Total.	M. p. of acid.	Correct m. p.
2 : 3	0.982	0.194	0.845	1.039	148—149°	149—150°
2 : 4	0.993	0.594	0.470	1.064	157—158	158—159
2 : 5	1.003	0.244	0.811	1.055	151—152	153—154
2 : 6	0.984	0.284	0.777	1.061	96—102	146—147
3 : 4	1.007	0.583	0.496	1.079	227—228	229—230
3 : 5	0.988	0.162	0.850	1.012	212—213	213—214

*Oxidation of the Dihalogen Compounds.*

## Series IV.

	Weight taken.	Acid.	Unchanged.	Total.	M. p. of acid.	Correct m. p.
1 h., 30 m. 135—140°	Cl : Cl	0.845	0.334	0.569	0.903	155—159°
	Cl : Br	1.029	0.406	0.706	1.112	157—160
	Br : Cl	1.016	0.416	0.676	1.092	125—133
	Br : Br	1.475	0.377	1.206	1.583	141—145

*Oxidation of the Dihalogen Compounds (continued).*

## Series V.

	2 : 4.	Weight taken.	Acid.	Unchanged.	Total.	M. p. of acid.	Correct m. p.
1 h., 30 m.	Cl : Cl	0·810	0·440	0·442	0·882	159—160°	160°
135—140°	Br : Cl	0·999	0·459	0·640	1·099	151—153	154—155
	Br : Br	1·408	0·672	0·871	1·543	155—158	158—159

## Series VI.

	2 : 5.						
1 h., 35 m.	Cl : Cl	0·806	0·225	0·593	0·818	135—140°	153°
135—140°	Cl : Br	1·014	0·209	0·861	1·070	150—152	155—156
	Br : Br	1·426	0·293	1·206	1·499	140—145	153—154

## Series VII.

	2 : 6.						
1 h., 30 m.	Cl : Cl	0·795	0·362	0·539	0·901	116—130°	139—140°
135—145°	Cl : Br	1·000	0·327	0·768	1·095	103—125	143—144
	Br : Br	1·423	0·538	1·006	1·544	90—118	146—147

## Series VIII.

	3 : 4.						
1 h., 30 m.	Cl : Cl	0·796	0·491	0·383	0·874	197—199°	200—201°
135—140°	Cl : Br	1·014	0·630	0·487	1·117	201—204	218
	Br : Cl	0·991	0·612	0·480	1·092	203—205	214
	Br : Br	1·416	0·595	0·934	1·529	224—226	229—230

## Series IX.

	3 : 5.						
1 h., 30 m.	Cl : Cl	0·811	0·106	0·708	0·814	183—184°	182—183°
135—140°	Cl : Br	0·995	0·118	0·891	1·009	191—192	189—190
	Br : Br	1·425	0·122	1·326	1·448	210—211	213—214

*Oxidation of the Monohalogen Compounds.*

## Series X.

Time, 30 minutes. Temperature, 140—148°.

	Weight taken.	Acid.	Unchanged.	Total.	M. p. of acid.	Correct m. p.
<i>o</i> -Cl	0·994	0·092	not determined		130—131°	137°
<i>m</i> -Cl	0·996	0·064	"	"	144—145	153
<i>p</i> -Cl	0·996	0·200	"	"	234—235	236
<i>o</i> -Br	1·334	0·388	"	"	137—140	148
<i>m</i> -Br	1·336	0·274	"	"	143—145	155
<i>p</i> -Br	1·338	0·766	"	"	242—244	251
<i>o</i> -I	1·718	0·102	"	"	147—148	162—163
<i>m</i> -I	1·728	0·142	"	"	175—177	187—188
<i>p</i> -I	1·738	0·139	"	"	263	265

*Oxidation of the Monohalogen Compounds (continued).*

## Series XI.

Time, 60 minutes. Temperature, 130—135°.

	Weight taken.	Acid.	Unchanged.	Total.	M. p. of acid.	Correct m. p.
<i>o</i> -Cl	1·000	0·107	0·803	0·910	132—134°	137°
<i>m</i> -Cl	0·989	0·091	0·895	0·986	146—148	153
<i>p</i> -Cl	1·003	0·170	0·802	0·972	235—236	236
<i>o</i> -Br	1·359	0·376	0·988	1·364	140—142	148
<i>m</i> -Br	1·358	0·303	1·020	1·323	150—152	155
<i>p</i> -Br	1·349	0·692	0·773	1·465	245—247	251
<i>o</i> -I	1·736	0·117	1·575	1·692	152—157	162—163
<i>m</i> -I	1·740	0·170	1·589	1·759	178—182	187—188
<i>p</i> -I	1·729	0·147	1·597	1·744	263—265	265

THE UNIVERSITY,  
LEEDS.CLXIV.—*The Composition of Beryl.*

By JAMES HOLMS POLLOK, B.Sc.

DURING a research on the extraction of glucina, and in the subsequent determination of the heat of formation of glucinum chloride, I noticed that this determination gave varying numbers for different samples of metal prepared from distinct portions of glucina, all of which appeared to be equally pure and free from alumina according to the ordinary chemical tests. Moreover, the anhydrous chloride behaved in a remarkable manner, for, without any apparent reason, the ratio of metal to chlorine was subject to wide variations which could not possibly be accounted for by the presence of a known element, as the most careful analysis failed to detect the presence of any other substance.

Although I was able to prepare a very well-defined specimen of pure white, crystalline, anhydrous glucinum chloride in tufts of long, silky needles, even this product did not give analytical data in agreement with the accepted atomic weight of glucinum. The results of two satisfactory duplicate analyses, in which the metal and chlorine found amounted almost exactly to the weight of chloride taken, gave:

Chlorine, 88·077. Glucinum, 11·99. Equivalent, 4·77,

this ratio being in close agreement with the older view of the equivalent of this element. An examination of Awdejew's analysis shows that he also experienced difficulty in getting concordant results with the chloride, and no chemist seems ever to have prepared a

chloride that gave results in accordance with the generally accepted equivalent 4.55 (compare *Ann. Chim. Phys.*, 1843, [iii], 7, 155).

All these points, together with the well-known anomalous specific heat of glucinum, led me to suspect that there was something in the composition of the beryl that had been so far altogether overlooked. I therefore decided to investigate the matter, and began by inquiring into the cause and extent of the variation in the composition of the anhydrous chlorides.

All the chlorides were prepared from basic carbonate or hydroxide of glucinum extracted from Limoges beryl, and purified from every trace of alumina and metals precipitable by ammonium sulphide. The samples gave absolutely no aluminium when tested by Haven's method of separation, they dissolved completely in ammonium carbonate, and gave no trace of a precipitate or darkening of colour when ammonium sulphide was added.

The dry basic carbonate or hydroxide was charred with eight times its weight of sugar, and then chlorinated in a stream of well-dried chlorine in a porcelain tube kept at a bright red heat by a special furnace, the chloride condensing in the cool end of the tube and then in a succession of glass globes. After chlorination was completed, a stream of well-dried carbon dioxide was swept through the apparatus to remove the excess of chlorine, and the product was quickly transferred from the tube and condensers to perfectly dry stoppered bottles or weighing tubes.

The analyses were as a rule performed by dissolving an unweighed quantity of the anhydrous chloride in distilled water and making up to a fixed volume of 250 c.c., and then taking two portions of 100 c.c. each, estimating the base by precipitation with ammonia in the one, and the chlorine by precipitation with silver nitrate in the other.

#### *Fractional Separation by Ammonium Carbonate.*

When every other method of separating alumina failed to indicate a trace, a solution of potassium hydrogen fluoride still gave a precipitate from a hydrofluoric acid solution, finally separating the last traces of this oxide and leaving a product spectroscopically free from aluminium. I therefore decided to make a fractional separation of a large quantity of glucina by ammonium carbonate, then remove every trace of alumina by potassium hydrogen fluoride, finally convert the glucina into anhydrous chloride, and take the equivalent of the glucina in each fraction to see whether they agreed or not, and, if not, in which fraction I must look for that glucina with a high atomic weight.

Fifty grams of basic glucinum carbonate free from iron were

digested for a week with 500 c.c. of saturated solution of ammonium carbonate, filtered, and the glucina precipitated by boiling, two fractions being thus obtained, a dissolved portion of 25 grams and an undissolved portion of 17.5 grams.

These, in turn, were each treated with 250 c.c. of ammonium carbonate, yielding four fractions, which, after drying and igniting, gave :

1st	Dissolved.	2nd	Dissolved	9.0	grams	marked	D.D.
	"	2nd	Undissolved	4.5	"	"	D.U.
1st	Undissolved.	2nd	Dissolved	6.4	"	"	U.D.
	"	2nd	Undissolved	2.5	"	"	U.U.

Each of those four fractions were now carefully purified from alumina by solution in hydrofluoric acid, precipitation by potassium hydrogen fluoride, filtration, and decomposition by sulphuric acid, the glucina being finally recovered and then converted into anhydrous chloride, the analyses of the different specimens of chloride giving the following series of results :

Sample.	Ignited oxide.	Silver chloride.	Percentage of		Equivalent.
			Metal.	Chlorine.	
D.D.....	0.172	1.753	14.58	85.42	6.05
" .....	0.172	1.754			
D.U. ....	0.167	1.755	13.91	86.09	5.73
" .....	0.169	1.755			
U.D. ....	0.204	2.127	13.91	86.09	5.73
" .....	0.200	2.127			
U.U. ....	0.0900	0.9545	13.36	86.64	5.47
" .....	0.0896	0.9525			

In every case the equivalent was much too high, and the concentration of the substance with high equivalent, although slight, was, if anything, in the most soluble portion, this result being the opposite of what I had anticipated. All these chlorides were obtained in white, crystalline tufts of needles with a shade of yellow ; they gave the reaction of glucinum and showed no trace of any other known element.

#### *Fractional Crystallisation of the Sulphate.*

Having failed to concentrate the heavy glucina satisfactorily by the use of ammonium carbonate, I next tried a number of experiments on the fractional crystallisation of the sulphate.

Glucinum sulphate has the formula  $\text{GISO}_4 \cdot 4\text{H}_2\text{O}$ , and, if the atomic weight of the metal be 9.1, it would have a percentage composition of  $\text{G} 10$ , 14.17 ;  $\text{SO}_3$ , 45.17 ;  $\text{H}_2\text{O}$ , 40.66.

On dissolving 40 grams of basic glucinum carbonate in excess of

sulphuric acid and crystallising under reduced pressure over sulphuric acid, I obtained two crops of 28 grams and 17 grams of sulphate, which were recrystallised, yielding in all four crops of crystals; these were weighed, and the ignition of a gram of each gave:

1st Crop.	1st.	12.04	grams sulphate with 14.6 per cent. $\text{GlO}$ .
„	2nd.	10.13	„ „ 14.4 „ „
2nd Crop.	1st.	6.50	„ „ 14.0 „ „
„	2nd.	5.45	„ „ 14.0 „ „

The results show that the heavy glucina tends to crystallise in the first fraction.

The second and third crops of crystals were always much finer than the first crop, a fact which suggests that these specimens might be purer. A quantity of about 2500 grams of crude glucinum sulphate was now crystallised out, and the first crop dissolved and recrystallised; 50 grams of the first crop of this second crystallisation were taken, and the glucina separated and converted into anhydrous chloride, which was obtained in beautiful tufts of needles with patches of a deep blue colour, changing to green at the extremity of the condenser. On analysis, the chloride gave:

Ignited oxide.	Silver chloride.	Percentage of		Equivalent.
		Metal.	Chlorine.	
0.278	2.472	18.73	81.27	8.17
0.275	2.432			

A sample of glucina prepared from sulphate which did not show an abnormal proportion of oxide was now converted into anhydrous chloride and analysed; it gave 12.28 per cent. of metal and 87.72 per cent. of chlorine, the equivalent being 4.96. Although still theoretically too high, this is much lower than that from the sulphate with high equivalent, and would indicate that a new substance is present.

#### *Examination of the Reprecipitated Bases.*

When most of the alumina had been removed from a mixture of alumina and glucina by crystallisation as alum, precipitation by alcohol, or saturation with gaseous hydrogen chloride, and the residual solution, after removal of excess of acid, was treated with a large excess of a solution of ammonium carbonate, the glucina was precipitated, but redissolved to a perfectly clear solution, and then after a time quite a heavy precipitate came down, and it occurred to me that the heavy glucina might possibly be co-precipitated with the alumina or whatever other substance was deposited.

A quantity of about 20 grams of reprecipitated hydroxides was

dissolved and treated with caustic soda to remove iron, then successively acidified with hydrochloric acid, precipitated by ammonia, dissolved in hydrofluoric acid, and the alumina precipitated with excess of potassium hydrogen fluoride. The residual liquid was evaporated to dryness, the glucinum fluoride decomposed by excess of strong sulphuric acid, dissolved in water, and the glucina and its analogue precipitated as hydroxide by ammonia, well washed and dried, then chlorinated in the ordinary way. The product had a slightly yellow colour, but showed no trace of blue or green, and the portion next to the charge separated in tufts of crystalline needles, whereas the part at the further end of the condenser was in the form of a flocculent powder. Analysis gave:

Ignited oxide.	Silver chloride.	Percentage of		Equivalent.
		Metal.	Chlorine.	
0.090	0.775	20.39	79.61	9.08
0.095	0.778			

To make perfectly sure that this high equivalent was not due to any accidental circumstance, the whole of the chloride thus prepared was precipitated as hydroxide, reconverted into chloride, and again analysed:

Ignited oxide.	Silver chloride.	Percentage of		Equivalent.
		Metal.	Chlorine.	
0.120	1.072	18.36	81.64	7.97
0.118	1.065			

Again, it was noticed that the first portion of the chloride formed tufts of needles, whilst further along the condenser it had separated in flakes.

In a second experiment, the tufts of needles, like glucinum chloride, were kept separate from the flaky deposit and analyses made on both samples. The least volatile, crystalline portion gave:

Ignited oxide.	Silver chloride.	Percentage of		Equivalent.
		Metal.	Chlorine.	
0.0156	0.1448	16.7	83.3	7.31
0.0154	0.1455			

The most volatile, amorphous portion gave:

Ignited oxide.	Silver chloride.	Percentage of		Equivalent.
		Metal.	Chlorine.	
0.0151	0.1011	27.47	72.53	14.8

A spectroscopic examination of this last product showed that the lines of glucinum, although still present, were becoming weaker, and

other lines, which were weak in all previous samples of glucina, were now becoming distinctly stronger.

*Fractional Distillation of the Chloride.*

To test the effect of the fractional distillation of the chloride, I chlorinated some glucina having the high equivalent and stopped the experiment soon after the anhydrous chloride began to distil over. The first portion of anhydrous chloride was raked out and the experiment continued, when separate analyses made of the first and second yields of chloride gave the following results :

First portion :

Ignited oxide.	Silver chloride.	Percentage of		Equivalent.
		Metal.	Chlorine.	
0.3620	2.759	23.38	76.62	10.81

Second portion :

Ignited oxide.	Silver chloride.	Percentage of		Equivalent.
		Metal.	Chlorine.	
0.440	4.507	14.47	85.53	5.99

Clearly the element with the high atomic weight is most readily converted into chloride and comes over freely in the earlier stages of the distillation.

I also made another fractional distillation of anhydrous chloride, but stopped the whole operation almost immediately the reaction began, and, when only a small proportion of chloride had distilled over, this fraction was collected in two portions and analysed :

Sample.	Ignited oxide.	Silver chloride.	Percentage of		Equivalent.
			Metal.	Chlorine.	
1st Condenser .....	0.1450	1.291	18.62	81.38	8.11
2nd Condenser.....	0.2100	1.122	34.70	65.30	18.74

As the tubes were perfectly dry, the number for the second portion must be regarded as correct, yet this sample gave the reactions of glucinum, but not those of any other element, so it would seem to indicate the existence of a new element analogous to glucinum and giving all the ordinary reactions of this metal, but having a much higher atomic weight. Of course, there is nothing to show that there is not still a good deal of glucinum in the sample, and, if so, the atomic weight would be proportionately higher, and, if pure, this new element might possibly have a very high atomic weight indeed. After replacing the chlorine generator and the condensers, the whole experiment

was continued, yielding three products in the porcelain tube and first and second condensers ; these gave on analysis :

Volatility.		Ignited oxide.	Silver chloride.	Percentage of		Equivalent.
				Metal.	Chlorine.	
1st Condenser	.....	0·249	2·5450	14·5	85·47	6·01
2nd	,,	0·256	1·9115	24·02	75·98	11·29
3rd	,,	0·086	0·6170	25·77	74·23	12·30

Apart from the marked increase of equivalent with volatility, it is clear from this experiment that the heavy glucina tends to distil over first, whilst the normal glucina collects in the less volatile fractions.

### *Spectroscopic Investigation.*

A careful examination of the spark spectrum of the various preparations showed that the substance had not been separated in a state of purity, and even in those samples with the highest equivalent the lines of glucinum were strongly marked, but certain lines that were only faintly visible in ordinary samples of glucina became much more intense, whilst the lines of glucinum became faint.

The approximate measurements of the lines that I noted in particular are :

3995 s.	3634 f.	3274 f.
3969 m. Ca.	3610 s.	3251 m.
3934 m. Ca.	3403 f.	3247 f.
3914	3322 m. Be.	3240 f.
3899	3302 s. Na (?)	3199 m.
3882	3281 m.	3154 m.
3643 f.		

If a sample of glucina is fractionally precipitated by potassium hydrogen fluoride, the two lines 3274 and 3247 are seen in the fourth fraction of the potassium hydrogen fluoride precipitate and not in the second fraction, and they remain in the least volatile or purest portion of the glucinum chloride and are not strongly marked in the most volatile portion containing the heavy glucinum chloride. They must therefore belong to some other element.

### *Conclusion.*

From these experiments, it would seem that the beryl from Limoges is a more complex mineral than formerly supposed, and in addition to glucinum contains at least one new element having in the main the chemical properties of glucinum, but a much higher equivalent. This

explains the progressive diminution in the accepted atomic weight of the element from 9.28 (Awdejew) to 9.05 (Krüss and Moraht). Each new observer removed more and more of the other element. It also explains satisfactorily the anomalous specific heat of glucinum, as without doubt the specific heat was taken on a sample of metal containing both elements, and then multiplied by the lower atomic weight in place of the mean atomic weight of the alloy. The peculiarity of the ammonium sulphide precipitate was pointed out by Krüss and Moraht, who suspected it to contain a new element, and I identified the presence of zinc or some analogous element in this precipitate. This observation was recently confirmed by Parson, who, however, seems satisfied that it really is zinc mixed with iron, whilst I incline to Krüss and Moraht's view that this precipitate possibly contains another rare element.

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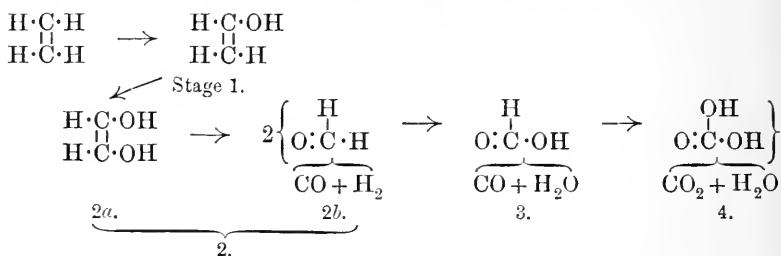
## CLXV.—*The Combustion of Ethylene.*

By WILLIAM ARTHUR BONE and RICHARD VERNON WHEELER.

THE present paper contains the results of an extension of our researches on combustion to the case of ethylene. Using the methods adopted in our previous work (Trans., 1902, 81, 536; 1903, 83, 1074; and this vol., p. 693), we have studied the combustion of the hydrocarbon (1) at 250—400°, under pressures varying from  $1\frac{3}{4}$  to  $2\frac{1}{2}$  atmospheres, in borosilicate glass bulbs; and (2) at 350—500°, under reduced pressure, in the circulation apparatus described in our previous paper.

The new results harmonise so completely with the view that the combustion of a hydrocarbon is essentially a process of hydroxylation, that we have adopted it as our working hypothesis throughout the paper. According to this theory, oxygen initially enters the hydrocarbon and is distributed between the carbon and hydrogen, giving rise to unstable hydroxylated molecules which, sooner or later, according to the rapidity of the process, undergo thermal decompositions into simpler products.

The main course of the combustion of ethylene may, we think, be represented by the following scheme:



It is difficult to summarise all the evidence that can be advanced in support of the foregoing theory; it is largely cumulative in character, and can best be judged after a perusal of the experimental part of the paper. The more salient features of our results may, however, be briefly stated as follows:

(1) There is no preferential combustion of either carbon or hydrogen when ethylene reacts with a quantity of oxygen insufficient to completely burn it to steam and oxides of carbon. The separation of carbon or of hydrogen, when it does occur, is to be entirely ascribed to secondary thermal decompositions.

(2) Formaldehyde is the most prominent intermediate oxidation product; at low temperatures, its formation is preceded by that of less oxygenated products.

(3) The formation of aldehydes precedes that of steam and oxides of carbon.

(4) The stage in the combustion process at which secondary decompositions set in is determined entirely by the temperature conditions. Below the ignition point, such changes do not come into play to any serious extent until Stage 3 is reached. The greater part of the formic acid,

$\begin{array}{c} \text{H} \\ | \\ \text{O} : \text{C} \cdot \text{OH} \end{array}$ , then decomposes into carbon monoxide and steam, whilst

the remainder is further oxidised to carbonic acid,  $\begin{array}{c} \text{OH} \\ | \\ \text{O} : \text{C} \cdot \text{OH} \end{array}$  (Stage 4),

which in turn breaks down into carbon dioxide and steam. Above the ignition point, the formaldehyde produced at Stage 2b (and conceivably also the dihydroxyethylene at Stage 2a) decomposes into carbon monoxide and hydrogen, so that, unless there is sufficient oxygen left over to burn these decomposition products, the apparent result is a preferential combustion of carbon, as, for example, when an equimolecular mixture of ethylene and oxygen is exploded.

(5) There is no separation of carbon or liberation of acetylene, even in the explosive combustion of ethylene, except when the oxygen present is insufficient to burn the hydrocarbon to formaldehyde. In such circumstances, the excess of ethylene is thermally decomposed, yielding carbon, hydrogen, methane, and traces of acetylene.

It was not to be expected that we should be able to identify the extremely unstable vinyl alcohol (which, according to the foregoing theory, should be formed at Stage 1) among our products. But there was evidence, in several of the bulb experiments, of the formation of the isomeric acetaldehyde. It seems to us reasonable to suppose that, under suitable conditions, part of the vinyl alcohol undergoes molecular change into the more stable acetaldehyde; the latter would then be independently further oxidised to carbon monoxide, steam, and formaldehyde, as proved in a previous paper (this vol., p. 724). The greater part, and often the whole, of the vinyl alcohol is very rapidly further oxidised to dihydroxyethylene, which at once breaks down into formaldehyde. There is no evidence that any part of the vinyl alcohol decomposes into acetylene and steam, a possibility suggested by H. E. Armstrong in his paper on the "Mechanism of Combustion" (Trans., 1903, 83, 1088).

We are not here immediately concerned with the precise way in which the oxygen is conveyed to the hydrocarbon (that is, whether directly or indirectly) at low temperatures. Until experiments have been made to test whether or not thoroughly dried mixtures of hydrocarbons and oxygen react below their ignition points, we prefer to reserve judgment in the matter. But we believe that at high temperatures (for example, in the explosion wave) the initial stage of the combustion involves the direct introduction of the oxygen molecule into the hydrocarbon; in other words, that there is a direct passage from  $\begin{smallmatrix} \text{H}\cdot\text{C}\cdot\text{H} \\ | \\ \text{H}\cdot\text{C}\cdot\text{H} \end{smallmatrix}$  to  $\begin{smallmatrix} \text{H}\cdot\text{C}\cdot\text{OH} \\ | \\ \text{H}\cdot\text{C}\cdot\text{OH} \end{smallmatrix}$  as the result of collisions between single molecules of ethylene and oxygen. It seems to us that the great advantage of the foregoing theory is that it supplies a rational view of all the facts, without supposing that there is any discontinuity between the slow and rapid combustion of a hydrocarbon.

#### EXPERIMENTAL.

The ethylene used in our experiments was sometimes prepared by Newth's method (Trans., 1901, 79, 915), but more usually by the interaction of ethyl alcohol and strong sulphuric acid at 160—170°.\* In the latter case, the gas was passed through (1) an empty worm cooled by

\* Explosion analyses of the gas obtained by Newth's method gave ratios  $C/A=1.02$  and  $1.01$ ; for the gas prepared from alcohol and sulphuric acid and subsequently purified by liquefaction, we obtained in a similar manner  $C/A=0.994$ ,  $0.998$ ,  $1.008$ ,  $1.011$ , and  $0.999$ , instead of the theoretical ratio  $1.000$ . It is, perhaps, hardly necessary to say that in such explosion analyses the explosive mixture,  $\text{C}_2\text{H}_4+3\text{O}_2$ , must be very largely diluted with inert gas. We always employed ratios, diluents/explosive mixture, between 4.0 and 4.5, and carried out the explosion under a pressure of about half an atmosphere.

ice, (2) a worm containing strong sulphuric acid, and (3) three worms containing a strong solution of caustic potash. The washed gas was further purified by repeated liquefaction and subsequent fractionation of the liquid.

The mixtures which were chiefly employed contained ethylene and oxygen in the ratios 2 : 1, 1 : 1, 1 : 2, and 1 : 4 respectively. They were made and stored in graduated glass holders over glycerine diluted with its own volume of water, a liquid in which the constituent gases are practically insoluble. After a particular mixture had remained in the holder for 12 hours, a sample of it was analysed; within the next 24 hours the remainder was either filled into the borosilicate glass bulbs, or transferred to the circulation apparatus, as circumstances required. The amounts of adventitious nitrogen in the mixtures were usually less than 0.3 and never more than 2.0 per cent. Following our usual custom, we shall leave this nitrogen out of the reckoning altogether and, except in one experiment in which a mixture of ethylene and air was used, shall always express the composition of our gaseous mixtures, as well as pressure records, in terms of the nitrogen free gas.

*Composition of Gaseous Products.*—Except in certain of the bulb experiments at 350—400°, when an explosion had occurred, the gaseous products never contained acetylene or any considerable amount of hydrogen. They consisted chiefly of the oxides of carbon, unchanged ethylene, aldehyde vapours, and sometimes also oxygen. Before proceeding to the analyses, we always removed aldehyde vapours by exposing the gases to sticks of zinc chloride for several hours. The various constituents were then removed and estimated by means of suitable absorbents in the following order: (1) carbon dioxide, (2) oxygen, (3) ethylene, and (4) carbon monoxide. There then usually remained, besides adventitious nitrogen, a very small quantity of a saturated hydrocarbon, and, in the case of the products from the circulation experiment, also some hydrogen. The analysis of this residual gas was in all cases carried out by exploding it with suitable proportions of oxygen and electrolytic gas. A special examination of the saturated hydrocarbon present proved it to be ethane, the ratio  $C/A$  obtained in its explosion analysis always being as nearly as possible 1.25. In several of the bulb experiments at 350—400°, an explosion occurred, and the gaseous products consisted chiefly of hydrogen and carbon monoxide, together with smaller quantities of carbon dioxide, methane, and occasionally also traces of acetylene. In such cases, after the carbon dioxide, unsaturated hydrocarbons, and carbon monoxide had been removed, in the order given, by suitable absorbents, the residual mixture of hydrogen and methane was analysed by explosion with excess of oxygen and air.

*The Interaction of Ethylene and Oxygen in Borosilicate Glass Bulbs at Temperatures between 250° and 400°.*

In these experiments the mixtures of ethylene and oxygen were sealed up, at atmospheric temperatures and pressures, in borosilicate glass bulbs, of about 70 c.c. capacity, which were afterwards kept at constant temperatures between 250° and 400°. The gases would, therefore, react under pressures varying from  $1\frac{3}{4}$  to  $2\frac{1}{2}$  atmospheres, according to the temperature conditions. The experimental method was substantially the same as that used in the previous researches on methane and ethane (*loc. cit.*), and need not, therefore, be further described. After the removal of the gaseous products, the bulbs were rinsed out with 2 or 3 c.c. of distilled water, and the rinsings tested for aldehydes both with Schiff's reagent and also with an ammoniacal solution of silver. Occasionally the iodoform test was also applied.

In recording the results, we shall in each case give (1) the temperature and pressure at which the bulbs were filled; (2) the duration of heating; (3) the "corrected" volume or pressure change, expressed either as "percentage contraction" or as pressure in mm. of mercury at constant volume, observed on opening the bulbs; (4) the composition of the "nitrogen-free" gaseous products, and (5) the ratio  $\text{CO}/\text{CO}_2$  in the products. We would again point out that, except in those cases in which an explosion occurred, the experiments were all carried out under conditions such as would entirely preclude the oxidation either of free hydrogen or of moist carbon monoxide.

*Experiments at 250°.*

At this temperature, ethylene and oxygen react with extreme slowness, even when they are mixed in equimolecular proportions, a ratio which the experiments at 300° showed to be on the whole the most favourable to rapid oxidation. Thus, for example, in the case of three bulbs (Nos. 1 to 3), filled, at 16° and 762 mm., with a mixture containing 49.5 volumes of ethylene to 50.5 volumes of oxygen, there was no visible change at 250° after 6 hours, although after 30 hours water appeared in all of them. One of the bulbs, when subsequently opened under mercury after being heated altogether for 94 hours, showed a contraction in volume of nearly 10 per cent., whilst the gaseous products contained  $\text{CO}_2 = 2.8$ ,  $\text{CO} = 4.0$ ,  $\text{C}_2\text{H}_4 = 47.0$ , and  $\text{O}_2 = 46.2$  per cent., but no acetylene. There was distinct evidence that an aldehyde had been formed, but not the slightest sign of any separation of carbon.

In the next experiment, two more bulbs (Nos. 4 and 5), originally filled, at 16° and 752 mm., with the foregoing mixture of ethylene

and oxygen, were kept at  $250^{\circ}$  for 8 days. The combustion was marked by the formation of aldehydes and steam, but there was neither separation of carbon nor liberation of either hydrogen or acetylene. The contractions observed when the cooled bulbs were opened under mercury were much larger than would be required for combustion to carbon monoxide, dioxide, and steam only, a circumstance which at once proves the formation of some soluble or condensable intermediate product. Analyses of the gaseous products in each case showed that, whereas practically the whole of the oxygen had disappeared, about two-fifths of the original ethylene remained intact at the end of the experiment. The results are tabulated below:

TABLE I.

Bulbs originally filled, at  $16^{\circ}$  and 762 mm., with  $\text{C}_2\text{H}_4 = 49.5$ ,  $\text{O}_2 = 50.5$ .

Bulb No.	4	5
Duration of heating.	8 days	8 days
Percentage contraction (corr.).*	36.1	35.6
Percentage composition of gaseous products.		
{ Carbon dioxide .....	21.6	20.8
{ Carbon monoxide ...	47.0	45.7
{ Oxygen .....	0.1	0.3
{ Ethylene .....	30.8	32.6
{ Ethane .....	0.5	0.6
CO/CO <sub>2</sub> .	2.17	2.20

\* For combustion to water and oxides of carbon only, without the intermediate formation of an aldehyde, these contractions would only have been 28.6 per cent.

This experiment, therefore, indicates that the combustion of ethylene is a process of essentially the same type as that which has been proved to occur in the cases of the saturated hydrocarbons methane and ethane. That is to say, there is no preferential combustion of either carbon or hydrogen, but, on the contrary, the oxygen becomes incorporated with the hydrocarbon molecule yielding intermediate products of an aldehydic character.

*Experiments at 300°.*

The rate of oxidation at this temperature was almost always very rapid when the gases had been originally mixed in equimolecular proportion. We have often observed equally fast rates with mixtures containing ethylene and oxygen in the ratio 2:1 (see Bulb No. 10, p. 1645), but on the whole these rates were rather slower than those usually found with equimolecular mixtures. The rate in each particular experiment was undoubtedly influenced by the "surface factor" of the bulb in which the gases were heated, so that it is inadvisable to lay much stress on variations in the rates of oxidation of different mixtures, unless a number of experiments show that these variations are considerable. Very much slower rates, however, were always observed with mixtures containing ethylene and oxygen in the ratio 1:2. This damping effect of an excess of oxygen over and above an equimolecular proportion, an effect equally well marked in the corresponding experiments with ethane, is easily explained by our theory.

*(1) With Equimolecular Mixtures.*

In this experiment three bulbs (Nos. 6—8), filled, at 15.5° and 750 mm., with a mixture containing 49.0 volumes of ethylene to 51.0 of oxygen, were kept at 300°, two of them for an hour and the third for 20 hours. The whole of the oxygen had disappeared within the hour; a more prolonged heating had little effect on the composition of the products, except to slightly lower the ratio  $\text{CO}/\text{CO}_2$ . Steam was formed, but there was again no separation of carbon. The contractions observed when the cooled bulbs were opened under mercury were again considerably greater than would be required for combustion to oxides of carbon and water only, and the rinsings from the bulbs gave strong aldehydic reactions. The gaseous products contained neither hydrogen nor acetylene, but we detected the presence of small quantities of ethane. The results are tabulated on p. 1644.

We may here comment on the small quantities of ethane almost invariably found in the gaseous products when the combustion proceeded normally, that is to say, without an explosion. We at first suspected that the original ethylene had contained some ethane as impurity, but this suspicion proved to be entirely groundless. At a later stage of the research, we found that small quantities of carbon monoxide and ethane may be obtained by heating ethylene with the vapour of formaldehyde at 300° in our bulbs; we therefore think the ethane in our products may be reasonably attributed to the interaction of ethylene and the formaldehyde which was undoubtedly the chief intermediate oxidation product.

TABLE II.

Bulbs originally filled, at  $15.5^{\circ}$  and 750 mm., with a mixture of 49.0 volumes of ethylene and 51.0 volumes of oxygen.

Bulb No.	6	7	8
Duration of heating.	1 hour	1 hour	20 hours
Percentage contraction (corr.).*	34.7	37.6	35.2
Percentage composition of gaseous products.	Carbon dioxide...	12.55	14.3
	Carbon monoxide	58.30	55.0
	Oxygen .....	0.30	nil
	Ethylene .....	27.80	29.3
	Ethane... ..	1.05	1.4
CO/CO <sub>2</sub> .	4.62	4.64	3.83

\* The percentage contraction for combustion to water and oxides of carbon only would have been 27.5.

(2) *Comparative Experiment with Mixtures containing Different Proportions of Ethylene and Oxygen.*

In this experiment six bulbs were used. Nos. 9 and 10 had been filled, at  $17^{\circ}$  and 760 mm., with a mixture  $2\text{C}_2\text{H}_4 + \text{O}_2$ ; Nos. 11 and 12, at  $15^{\circ}$  and 762 mm., with a mixture of the gases in equimolecular proportion; and Nos. 13 and 14, at  $17^{\circ}$  and 760 mm., with a mixture of 1 vol. of ethylene to 2 vols. of oxygen. The six bulbs were kept at  $300^{\circ}$  for 30 minutes and then rapidly cooled to the ordinary temperature. Water condensed on the inner surface of the four bulbs Nos. 9 to 12, and all four showed contractions in volume when subsequently opened under mercury. In the case of one of the two bulbs originally filled with the mixture  $2\text{C}_2\text{H}_4 + \text{O}_2$ , there had been a considerable disappearance of oxygen; the same remark applies also to both of the bulbs originally filled with the equimolecular mixture.

In the cases of bulbs Nos. 13 and 14, originally filled with the mixture  $\text{C}_2\text{H}_4 + 2\text{O}_2$ , a very interesting result was obtained. Although there were no visible signs of steam formation in either of them, the rinsings from both showed a pronounced aldehydic reaction, and there was only a very small contraction when the bulbs were opened under mercury. The gaseous products, however, contained no measurable quantity of either carbon monoxide or dioxide. Apparently,

therefore, interaction had occurred to a slight extent in each case, an aldehyde had been formed, but without any appreciable production of steam or oxides of carbon.

The results of this experiment are tabulated below:

TABLE III.

All bulbs originally filled at 15—17° and 760—762 mm.

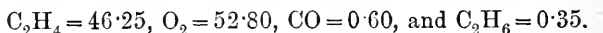
Bulb No.	9	10	11	12	13 and 14
Original mixture.	$2C_2H_4 + O_2$		$C_2H_4 + O_2$		$C_2H_4 + 2O_2$
Percentage contraction.	6.7	27.1	19.3	40.0	Very small.
Percentage composition of gaseous products.	Carbon dioxide..	0.50	4.70	5.10	10.0
	Carbon monoxide	1.20	23.75	17.55	65.8
	Oxygen .....	31.70	7.35	36.00	nil
	Ethylene .....	66.60	63.50	40.90	17.5
	Ethane .....	nil	0.70	0.45	6.5
Formation of aldehyde observed without any appreciable production of $CO_2$ , $CO$ , and $H_2O$ .					
$CO/CO_2$ .	2.4	5.08	3.44	6.58	

In the case of bulb No. 12, there had been a particularly fast rate of oxidation and a considerable accumulation of aldehydic vapours. This circumstance probably accounts for the presence of so much as 6.5 per cent. of ethane in the products, which, it will also be observed, is accompanied by an abnormally high ratio  $CO/CO_2$  (compare this with the results for bulbs Nos. 6—8 inclusive, originally filled with the mixture  $C_2H_4 + O_2$  and heated at 300°, where the ratio is only 3.83—4.64).

The observation made with bulbs 13 and 14, namely, that the formation of an aldehyde precedes that of steam or oxides of carbon, was, at a later stage of the research, strikingly confirmed by the following experiment.

A bulb (No. 15), which proved to be an extremely slow one, originally filled, under atmospheric pressure, with a mixture containing 49.1 and 50.9 per cent. of ethylene and oxygen respectively, was kept for an hour at 300—310°. There was no visible condensation of steam on cooling, and but little contraction (certainly not more than 1 per cent.) was observed when the bulb was subsequently opened under mercury. The gaseous products, however, had an extremely pungent aldehydic smell, and the rinsings from the bulb gave a very

strong aldehydic reaction with Schiff's reagent, and also instantly reduced an ammoniacal solution of silver. The gases produced no turbidity with a clear solution of barium hydroxide, and after the removal of aldehyde vapours by long contact with sticks of zinc chloride, they were found to have the following percentage composition:



The relative proportions of ethylene and oxygen in the gases suggests the formation, besides formaldehyde, of a certain amount of some less oxygenated product.

(3) *Experiment with a Mixture  $\text{C}_2\text{H}_4 + 2\text{O}_2$ .*

In this experiment two bulbs filled, at  $16^\circ$  and 760 mm., with a mixture of ethylene (1 vol.) and oxygen (2 vols.), were kept at  $300^\circ$  for 20 hours. In each case practically all the oxygen had disappeared. The rinsings from the bulbs still gave distinct aldehydic reactions, and the contractions observed when the bulbs were opened under mercury were still appreciably greater than those required for combustion to water and oxides of carbon only. The results are shown below:

TABLE IV.

Bulb No.	16	17
Percentage contraction (corr.).*	40.0	39.0
Percentage composition of gaseous products.		
Carbon dioxide.....	29.5	29.0
Carbon monoxide.....	66.7	66.1
Oxygen .....	0.3	1.7
Ethylene .....	2.5	2.2
Ethane .....	1.0	1.0
CO/CO <sub>2</sub> .	2.26	2.28

\* The contraction calculated for combustion to water and oxides of carbon would amount to about 36.75 per cent only.

(4) *Experiment with a Mixture  $\text{C}_2\text{H}_4 + 4\text{O}_2$ .*

Two bulbs, Nos. 18 and 19, filled, at  $18^\circ$  and 758 mm., with a mixture containing 19.6 and 80.4 per cent. of ethylene and oxygen respectively, were kept at  $300^\circ$ , the one for 6 hours, and the other for 70 hours. A large amount of change had occurred in 6 hours, although it will be seen that an appreciable amount of ethylene still survived

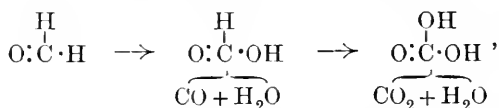
after 70 hours. The rinsings from both bulbs still gave distinct aldehydic reactions, showing the persistency of the aldehyde even in presence of large excess of oxygen. The results are tabulated below :

TABLE V.

Bulb No.		18	19
Duration of heating.		6 hours	70 hours
Percentage contraction (corr.).		19.3	25.8
Percentage composition of gaseous products.	Carbon dioxide .....	11.2	15.8
	Carbon monoxide .....	30.3	32.4
	Oxygen .....	55.7	50.2
	Ethylene .....	2.8	1.2
	Ethane.....	nil	0.4
CO/CO <sub>2</sub> .		2.70	2.05

A very remarkable feature of this experiment is the high ratio CO/CO<sub>2</sub> in the products, in spite of the fact that the oxygen originally present was greatly in excess of the amount required to completely burn the whole of the hydrocarbon to carbon dioxide and steam. What, then, is the explanation of this very large proportion of carbon monoxide in the products? In discussing this question, it must be remembered (1) that the experimental conditions preclude, on the one hand any oxidation of moist carbon monoxide, or, on the other hand, a reduction of carbon dioxide by either hydrogen or a hydrocarbon (Trans., 1902, 81, 538), and (2) that the formation of the aldehyde precedes that of steam or oxides of carbon. Our circulation experiments prove that the chief intermediate product in the combustion of ethylene is formaldehyde, and it is to the further oxidation of this substance that we must ascribe the final production of carbon monoxide, dioxide, and steam. Now if formaldehyde is directly burnt to these products, without the intermediate formation of hydroxylated molecules, we should certainly not expect a high ratio CO/CO<sub>2</sub> in the presence of a large excess of oxygen. On the contrary, under such conditions we should, from the kinetic standpoint, expect the bimolecular change,  $\text{CH}_2\text{O} + \text{O}_2 = \text{CO}_2 + \text{H}_2\text{O}$ , to predominate over the more complex trimolecular reaction,  $2\text{CH}_2\text{O} + \text{O}_2 = 2\text{CO} + 2\text{H}_2\text{O}$ . But if, on the other hand, we regard the oxidation of formaldehyde as a process of

hydroxylation, during which the unstable molecules,  $\text{O}:\overset{\text{OH}}{\underset{|}{\text{C}}}\cdot\text{H}$  and  $\text{O}:\overset{\text{OH}}{\underset{|}{\text{C}}}\cdot\text{OH}$ , are successively produced and decomposed, thus:



the difficulty of explaining the high ratio  $\text{CO}/\text{CO}_2$  disappears. For, in such a sequence of changes, the ratio  $\text{CO}/\text{CO}_2$  would largely depend on the stability of formic acid,  $\text{O}:\overset{\text{H}}{\underset{|}{\text{C}}}\cdot\text{OH}$ , at the particular temperature.

In other words, the hydroxylation theory would lead us to suppose that at a given temperature a certain proportion of formic acid at once breaks down into carbon monoxide and steam, whilst the remainder is further oxidised to carbonic acid,  $\text{O}:\overset{\text{OH}}{\underset{|}{\text{C}}}\cdot\text{OH}$ , which in turn breaks down into carbon dioxide and steam. It follows, therefore, that for a given original mixture of ethylene and oxygen, the ratio  $\text{CO}/\text{CO}_2$  in the final products should increase as the experimental temperature rises, since the stability of formic acid would obviously diminish. Now this is, as a matter of fact, just what we find whenever the combustion proceeds normally, that is to say without explosion, to the end. Thus, for the equimolecular mixtures of ethylene and oxygen we find, at  $250^\circ$ , a ratio  $\text{CO}/\text{CO}_2 = 2.2$  (Table I, p. 1642), at  $300^\circ$ , ratios varying between 3.8 and about 4.6 (Table II, p. 1644), whilst for a bulb at  $380^\circ$  (No. 20, see below) the ratio was about 7.6.

#### *Experiments at $350^\circ$ to $400^\circ$ .*

Above  $350^\circ$  the rate of oxidation of ethylene is so fast that unless we selected a very slow bulb, or diluted the mixture with nitrogen, an explosion occurred, the result being that the primary oxidation products were completely decomposed. Nevertheless, the experiments are of interest in that they seem to throw some light on the character of the explosive combustion of hydrocarbons.

#### *(1) With Equimolecular Mixtures.*

The mixture used in these experiments contained 49.1 and 50.9 per cent. of ethylene and oxygen respectively.

(a) A bulb (No. 20), filled at  $16^\circ$  and 748 mm., was kept at  $380^\circ$  for 30 minutes. Very little water condensed on cooling, and when the bulb was subsequently opened under mercury, the products were

found to be under great pressure. There had been absolutely no separation of carbon, and the rinsings from the bulb did not give any aldehydic reaction. The gaseous products, which contained no acetylene, had the following percentage composition :

$$\text{CO}_2 = 1.25 ; \text{CO} = 50.65 ; \text{H}_2 = 47.5 ; \text{CH}_4 = 0.6.$$

(b) In the next experiment the apparatus was so arranged that the bulbs could be watched during the whole time of heating. Three bulbs (Nos. 21—23), originally filled with the above mixture at  $16^\circ$  and 753 mm., were put into the bath at  $400^\circ$ . After the lapse of between 1 and 2 minutes an explosion occurred \* in all three bulbs, but without any separation of carbon. The capillary ends of two of the bulbs were fractured by the force of the explosion, but the third bulb remained intact. It was quickly removed from the bath, and after it had cooled only a very slight dew could be seen on its inner surface. On nipping off the sealed end of the capillary tube inside an india-rubber joint connected with a capillary manometer, the products were found to be approximately under 1420 mm. pressure. The rinsings from the bulb did not give any aldehydic reaction, and the gaseous products, which again contained no acetylene, had the following percentage composition :

$$\text{CO}_2 = 1.20 ; \text{CO} = 50.25 ; \text{CH}_4 = 1.00 ; \text{H}_2 = 47.55.$$

(c) In order to decide whether the combustion would proceed normally, if an explosion were prevented by retarding the primary oxidation, we next filled a very slow bulb (No. 24), at  $11.2^\circ$  and 753 mm., with the mixture used in the two previous experiments. On placing it in the air-bath at  $380^\circ$  no explosion occurred. After 15 minutes it was removed and cooled, when a large amount of water condensed. On opening the bulb under mercury, we found a contraction (corr.) of 36.2 per cent. The rinsings from the bulb showed a strong aldehydic reaction ; there had been no separation of carbon, and the gaseous products, which had the following percentage composition, contained only a trace of hydrogen :

$$\begin{aligned} \text{CO}_2 &= 8.65 ; \text{CO} = 66.20 ; \text{O}_2 = 0.50 ; \text{C}_2\text{H}_4 = 19.20 ; \text{C}_2\text{H}_6 = 5.00 ; \\ \text{H}_2 &= 0.45. \quad \text{Ratio, CO/CO}_2 = 7.65. \end{aligned}$$

In the slower bulb, therefore, the combustion had run its normal course.

(d) We next damped the rate of combustion by dilution with nitrogen. Two bulbs (Nos. 25 and 26) were filled, the one at  $19^\circ$

\* The dimensions of our bulbs were too small to allow of the "explosion wave" being set up ; by the term "explosion" we mean the initial stage of the explosion before the explosion wave (detonation) is set up.

and 767 mm., the other at 17.5° and 759 mm., with a mixture of ethylene and air containing 15.65, 17.65, and 66.70 per cent. of ethylene, oxygen, and nitrogen respectively. No. 25 was subsequently kept at 410° for 30 minutes, and No. 26 at 395° for an hour. No explosion occurred in either case, and much moisture condensed on cooling; there was no separation of carbon. On opening the bulbs under mercury, contractions of 13.3 and 12.5 per cent. respectively (equal to about 40 and 37.5 per cent. on the original "nitrogen-free" mixture) were observed. The rinsings from the bulbs gave a strong aldehydic reaction, and the products contained neither acetylene nor hydrogen.

The details of the experiment are shown below :

TABLE VI.

Bulb No.		25	26
Temperature.		410°	395°
Duration of heating.		30 minutes	1 hour
Percentage contraction (corr.).		13.3	12.5
Percentage composition of gaseous products.	Carbon dioxide .....	2.25	2.55
	Carbon monoxide .....	12.70	15.40
	Ethylene .....	5.40	4.30
	Ethane .....	2.50	1.15
	Nitrogen.....	77.15	76.60
CO/CO <sub>2</sub> .		5.64	6.04

These experiments show, therefore, that provided the rate of the primary oxidation be damped, either by using a very slow bulb or by dilution of the reacting mixture with an inert gas, the combustion will proceed normally to the end, and there will be neither liberation of hydrogen nor deposition of carbon. But, on the other hand, the velocity of the primary oxidation is usually so great at these temperatures that the mixture is locally heated to the temperature at which an explosion is set up. The result is that the final products are composed of practically equal volumes of carbon monoxide and hydrogen, as though there had been a preferential combustion of carbon, thus:  $C_2H_4 + O_2 = 2CO + 2H_2$ .

A similar preferential combustion of carbon apparently occurs when

the explosion wave traverses a long leaden coil containing a mixture of ethylene and oxygen in equimolecular proportions. Thus Lean and Bone (*Trans.*, 1892, 61, 886), on exploding a mixture containing 49.41, 47.69, and 2.90 per cent. of ethylene, oxygen, and nitrogen respectively, found an increase in pressure of from 747 to 1503 mm., whilst the gaseous products contained:

$\text{CO}_2 = 0.33$ ,  $\text{CO} = 49.11$ ,  $\text{H}_2 = 48.78$ ,  $\text{CH}_4 = 1.01$ , and  $\text{N}_2 = 1.01$  per cent.

We are thus led to ask whether at higher temperatures above the ignition point the combustion of ethylene takes an entirely different course from that which it certainly follows at temperatures below the ignition point. We can hardly believe that there is any such discontinuity, and in forming this opinion we have been guided by the following considerations.

Our circulation experiments prove that formaldehyde is the chief intermediate product of the combustion of ethylene at low temperatures, and, in a series of hitherto unpublished experiments, we have proved that at  $500^\circ$  and upwards formaldehyde is rapidly decomposed in accordance with the equation  $\text{CH}_2\text{O} = \text{CO} + \text{H}_2$ .

Thus, for example, when formaldehyde vapour was admitted to a vacuum porcelain tube heated uniformly to  $700^\circ$ , it was almost instantly decomposed, the gaseous products containing:

$\text{CO}_2 = 0.4$ ,  $\text{CO} = 50.25$ ,  $\text{H}_2 = 48.7$ , and  $\text{CH}_4 = 0.65$  per cent.

The decomposition products of formaldehyde have, therefore, exactly the same composition as the products obtained when an equimolecular mixture of ethylene and oxygen is exploded, either in a small glass vessel or in a long leaden coil. This identity of composition may be a mere coincidence, but it is difficult to resist the conclusion that there is some connection between the two sets of facts. The connection is supplied if we assume that even the explosive combustion of ethylene involves the momentary formation and decomposition of formaldehyde, a process which may be empirically expressed as follows:



We must distinguish between the conditions existing in an ethylene flame, or in the initial stage of the explosion of ethylene and oxygen, and the conditions existing in the explosion wave (detonation). In the latter case, the existence of intermediate oxidation products would be merely momentary, the duration of their existence probably being small in comparison with the mean time between the molecular impacts concerned in the propagation of the wave.\*

\* H. B. Dixon (*Phil. Trans.*, 1893, 184, Series A, 97) found, as the mean of four determinations, that the explosion wave was propagated through an equimolecular mixture of ethylene and oxygen at a rate of 2507 metres per second.

(2) *With Mixtures of 2 Volumes of Ethylene to 1 Volume of Oxygen.*

These mixtures also exploded at temperatures above  $350^{\circ}$ , although the violence of the explosion was considerably less than was the case with the equimolecular mixtures.

Three bulbs (Nos. 27—29) filled, at  $22^{\circ}$  and 760 mm., with a mixture  $2\text{C}_2\text{H}_4 + \text{O}_2$ , were separately heated, the first at  $360^{\circ}$ , the second at  $380^{\circ}$ , and the third at  $400^{\circ}$ . After the lapse of from  $2\frac{1}{4}$  to about 4 minutes there appeared in each case a bright flash accompanied by a dense cloud of carbon particles. On cooling the bulbs, a little water condensed, and the gaseous products were found to be under pressures of from 1087 to 1200 mm. The rinsings from the bulbs gave no aldehydic reaction; the products, which had a tarry odour, were composed of hydrogen (about one-half), carbon monoxide (about one-third), and methane, besides smaller quantities of carbon dioxide and unsaturated hydrocarbons, including traces of acetylene. The results of this experiment are tabulated below.

TABLE VII.

Bulbs originally filled, at  $22^{\circ}$  and 760 mm., with a mixture  $2\text{C}_2\text{H}_4 + \text{O}_2$ .

Bulb No.		27	28	29
Temperature.		$360^{\circ}$	$380^{\circ}$	$400^{\circ}$
Time at which explosion occurred.		3 mins. 5 secs.	about 3 mins.	2 mins. 20 secs.
Pressure of gaseous products.		1114 mm.	1087 mm.	1200 mm.
Percentage composition of gaseous products.	Carbon dioxide ...	2.3	2.5	1.7
	Carbon monoxide	32.7	32.7	33.3
	Hydrogen .....	52.3	49.7	53.8
	Unsaturated hydrocarbons (including acetylene)	2.5	3.5	2.0
	Methane .....	10.2	11.6	9.2

The experiment shows that the main reaction,  $\text{C}_2\text{H}_4 + \text{O}_2 = [2\text{CH}_2\text{O}] = 2\text{CO} + 2\text{H}_2$ , had been accompanied by the thermal decomposition of the excess of ethylene into carbon, hydrogen, and methane, together with traces of acetylene. The separation of carbon was, therefore, entirely a secondary effect.

(3) *With a Mixture of 1 Volume of Ethylene with 2 Volumes of Oxygen.*

Five bulbs (Nos. 30 to 34), filled with a mixture  $C_2H_4 + 2O_2$ , at  $17^\circ$  and 759 mm., were separately heated at various temperatures between  $375^\circ$  and  $400^\circ$ . Three of them exploded after about 3 minutes and were fractured by the force of the explosion. In the case of the two remaining bulbs, there had been a slower combustion, and therefore no explosion; they were heated altogether 10 minutes, and then rapidly cooled. Water condensed, and considerable contractions were observed when the bulbs were opened under mercury. The rinsings in each case showed a distinct aldehydic reaction, and the composition of the gaseous products showed that combustion had followed the normal course. We need only give the details for one bulb (No. 34), in which practically the whole of the oxygen disappeared during the 10 minutes' heating. The percentage contraction observed was 37.6, and the gaseous products had the following percentage composition:

$CO_2 = 24.0$ ;  $CO = 71.0$ ;  $O_2 = 0.6$ ;  $C_2H_4 = 2.0$ ;  $C_2H_6 = 0.8$ ;  $H_2 = 1.6$ .  
 Ratio,  $CO/CO_2 = 2.96$ .

*Experiment with a Large Bulb at  $300-350^\circ$ .*

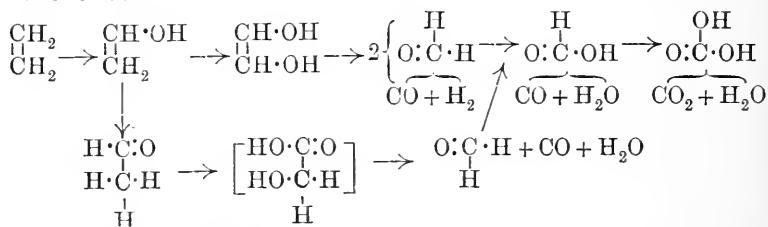
According to the hydroxylation theory, the primary oxidation product of ethylene should be vinyl alcohol,  $CH(OH):CH_2$ . This substance is so extremely unstable, however, that it does not seem ever to have been definitely isolated. At the moment of its formation it is apparently always transformed into the isomeric acetaldehyde. In the circulation experiments, where, as we shall see, ethylene is burnt under reduced pressure, we were never able to obtain any evidence of the presence of acetaldehyde in the products. The rinsings from one or two of the bulb experiments, however, gave a distinct iodoform reaction, and there was also some evidence, from the composition of the gaseous products, of the formation of less oxygenated products than formaldehyde. We therefore decided to try a bulb experiment on a larger scale than usual, as follows: a large borosilicate glass bulb of 485 c.c. capacity (equal in size to about 7 of the smaller bulbs) was filled, at  $17^\circ$  and 757 mm., with a mixture containing 49.1 and 50.9 per cent. of ethylene and oxygen respectively. After sealing the capillary ends of the bulb, it was placed in an air-bath at  $300^\circ$ . The temperature was kept at  $300-310^\circ$  for  $2\frac{3}{4}$  hours, and then during the next  $1\frac{1}{2}$  hours was slowly raised to  $350^\circ$ , when the bulb was removed and allowed to cool. Much water condensed, and, on opening the bulb at  $17.5^\circ$  in connection with a capillary manometer, the dry products were found to be under 455 mm.

pressure. There had thus been a fall in pressure of 302 mm., or practically 40 per cent., during the experiment. The products had an extremely pungent aldehydic smell, and on rinsing out the bulb with water a strongly aldehydic solution was obtained. This liquid gave the iodoform reaction, and contained acetaldehyde, as well as formaldehyde, but no ethyl alcohol. It gave no precipitate with a solution of magnesium chloride, and therefore did not contain ethylene oxide. The gaseous products had the following percentage composition:

$$\text{CO}_2 = 15.75; \text{CO} = 53.75; \text{C}_2\text{H}_4 = 29.10; \text{C}_2\text{H}_6 = 1.40.$$

$$\text{Ratio, CO/CO}_2 = 3.4.$$

For combustion to water and oxides of carbon only, the contraction would have been 208 mm. instead of the 302 mm. observed, a circumstance which points to a large accumulation of aldehydes during the experiment. The experiment was repeated and the presence of acetaldehyde in the products confirmed. Moreover, it is difficult to account for the composition of the gaseous products in the above experiment on the supposition that formaldehyde was the only soluble or condensable intermediate product; the results would be more satisfactorily explained if we assume the formation of some less oxygenated product than formaldehyde. It is probable that, under the conditions of the bulb experiments, where the gases react under considerable pressures, and the primary oxidation products rapidly accumulate in the system, a portion of the vinyl alcohol may be transformed into the isomeric acetaldehyde,  $\text{CH}(\text{OH})\text{:CH}_2 \rightarrow \text{CH}_3\cdot\text{CHO}$ , which then undergoes independent oxidation to carbon monoxide, steam, and formaldehyde, as proved in a previous paper (this vol., p. 724). The remainder of the vinyl alcohol is rapidly further oxidised to the unstable dihydroxyethylene, which at once decomposes into formaldehyde. The whole scheme of combustion, under the conditions of the bulb experiments, may be represented as follows:



*Experiments with Mixtures of Ethylene and Oxygen in the Circulation Apparatus.*

These experiments were undertaken in order that we might follow more closely the main course of the combustion process. A

description of the circulation apparatus has been given in an earlier paper on methane (Trans., 1903, 83, 1074). The reacting gases were continuously circulated, under reduced pressure, over a heated surface of porous porcelain at a constant rate throughout a given experiment. Soluble or condensable intermediate products were quickly removed from the sphere of action by the water contained in the worm and spiral of the apparatus. Moreover, not more than 1/50th of the gas in the apparatus would be in the heated zone at any one time, and of this only a small fraction would actually be in contact with the catalysing surface. The conditions under which the combustion took place were, therefore, very different from those which prevailed in the bulb experiments, where the gases reacted under considerable pressures, and the primary oxidation products accumulated within the sphere of action. Moreover, the conditions of the circulation experiments admitted of the rapid oxidation of hydrogen or of carbon monoxide.

Following our usual plan, we shall give in each case (1) the pressure of the dry "nitrogen-free" mixture, at the ordinary temperature  $t^\circ$ , introduced into the cold apparatus, (2) its pressure after the furnace had been lighted and the combustion tube raised to the experimental temperature  $T^\circ$ , (3) the "corrected" pressures of the dry "nitrogen-free" gases in the apparatus at regular intervals of time during the combustion, (4) the pressure of the dry "nitrogen-free" products at the end of the experiment, after the furnace had been turned out and the apparatus had again cooled down to the ordinary temperature, and (5) the percentage composition of the gaseous products.

### 1st Experiment.

This extended over  $2\frac{3}{4}$  days, the temperature of the combustion tube varied between  $405^\circ$  and  $410^\circ$  throughout, and the rate of circulation was fairly rapid, the circuit being completed once in about every 40 minutes.

The original mixture contained 49.0 and 51.0 per cent. of ethylene and oxygen respectively.

Pressure of the cold dry "nitrogen-free"	
original mixture at $16.2^\circ$ .....	= 479.5 mm.
Pressure of the cold dry "nitrogen-free"	
final products at $16.2^\circ$ .....	= 277.8 mm.

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Total fall in pressure = 201.7 mm.  
or 42.7 per cent.

The daily records were as follows:  $T$  = temperature of combustion

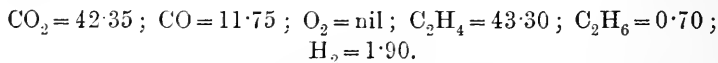
tube;  $t$  = temperature of the main body of gas in the apparatus;  
 $P$  = corrected pressure of the dry nitrogen-free gas in mm.

Day.	$T$ .	$t$ .	$P$ .
0 .....	407° .....	19·8° .....	508·8 mm.
1 .....	405 .....	22·8 ..	381·4 „
2 .....	407 .....	23·6 .....	309·2 „
2 $\frac{3}{4}$ .....	410 .....	23·0 .....	293·8 „

The pressure curve for this experiment, which is shown in Fig. 1 (p. 1657), Curve II (ordinates = pressure in cm., abscissæ = time in days), is quite regular throughout, the combustion slackening somewhat towards the end.

There was no deposition of carbon on the white surface of the porous porcelain with which the combustion tube was packed, a remark which applies also to all the other circulation experiments. The liquid in the worm, which would contain all the soluble and condensable products of combustion, was perfectly transparent and neutral. It had a strong aldehydic smell and reaction, but gave neither the iodoform reaction nor a precipitate with a neutral solution of magnesium chloride. It therefore contained neither acetaldehyde nor ethylene oxide. The aldehyde present consisted entirely of formaldehyde, which was identified both by its *p*-bromophenylhydrazone and by its characteristic white thio-derivative (see Drugman and Stockings, Proc., 1904, 20, 115). On careful evaporation in a glass basin over a water-bath, the liquid left the faintest possible greasy residue, but a solution of this in water did not give any aldehydic reaction. Moreover, the liquid certainly contained no glyoxal.

The percentage composition of the "nitrogen-free" gaseous products was as follows:



The hydrogen had undoubtedly been produced as the result of the thermal decomposition of formaldehyde,  $\text{CH}_2\text{O} = \text{CO} + \text{H}_2$ . Comparing now the partial pressures of the ethylene and oxygen in the original mixture with those of the various gaseous products at the end of the experiment, we obtain the following numbers:

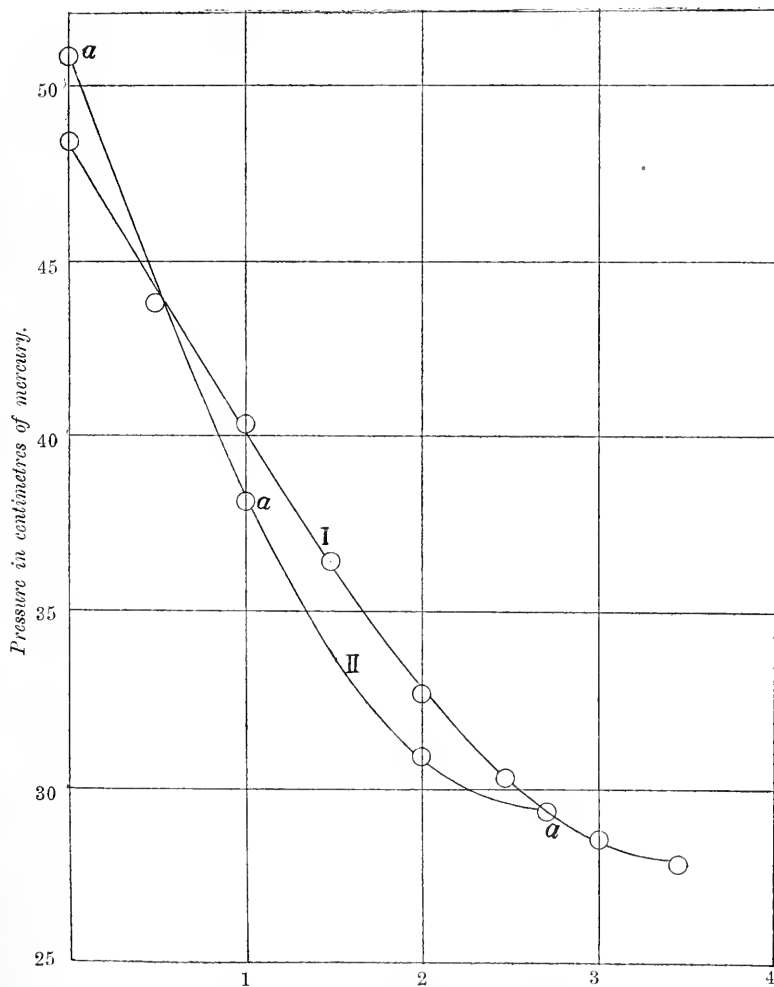
*Original Mixture.*

Ethylene..... 234.8 mm.      Oxygen..... 244.7 mm.

*Products.*

Carbon dioxide.....	117.6 mm.	Ethylene...	120.5 mm.
Carbon monoxide...	32.6 „	Ethane ...	1.9 „
		Hydrogen..	5.2 „

FIG. 1.



Thus, 112.4 mm. (that is,  $234.8 - 120.5 - 1.9$ ) of ethylene had been burnt during the experiment, yielding only 150.2 mm. of carbon

monoxide and dioxide. Assuming the 5.2 mm. of hydrogen to have been formed by the thermal decomposition of a corresponding quantity of formaldehyde vapour, and the 1.9 mm. of ethane by the interaction of ethylene and formaldehyde,  $\text{CH}_2\text{O} + \text{C}_2\text{H}_4 = \text{CO} + \text{C}_2\text{H}_6$ , we calculate that of the 112.4 mm. of ethylene burnt, 71.5 mm. were represented in the products by steam and oxides of carbon, and the remaining 40.9 mm., or as much as 36.5 per cent. of the whole, by formaldehyde or its decomposition products. We will now show that this conclusion agrees very well with the amount of oxygen which actually disappeared during the experiment, namely, 244.7 mm.

58.8 mm. of $\text{C}_2\text{H}_4$ burnt to	$2\text{CO}_2 + 2\text{H}_2\text{O}$	would require	176.4 mm. $\text{O}_2$
12.7       "       "       "	$2\text{CO} + 2\text{H}_2\text{O}$	"       "	25.4       "
40.9       "       "       "	$2\text{CH}_2\text{O}$	"       "	40.9       "
Total.....			242.7 mm.

### 2nd Experiment.

On repeating the previous experiment, we obtained a very similar result. The mixture used contained 49.8 and 50.2 per cent. of ethylene and oxygen respectively. The temperature of the combustion tube was practically the same as in the previous experiment, but the rate of circulation was somewhat slower, the circuit being completed once in every hour.

Pressure of the dry nitrogen-free	
original mixture at $19.8^\circ$ .....	= 454.0 mm.
Pressure of the dry nitrogen-free	
final products at $19.8^\circ$ .....	= 270.5 mm.

---

Fall = 183.5 mm. or 40.5 per cent.

Records were taken every 12 hours throughout the experiment, as follows :

Day.	<i>T</i> .	<i>t</i> .	<i>P</i> .
0 .....	405° .....	24.0° .....	482.9 mm.
$\frac{1}{2}$ .....	401 .....	25.0 .....	438.0   "
1 .....	400 .....	22.6 .....	403.6   "
$1\frac{1}{2}$ .....	403 .....	27.0 .....	360.4   "
2 .....	405 .....	26.4 .....	326.7   "
$2\frac{1}{2}$ .....	404 .....	26.0 .....	302.8   "
3 .....	403 .....	26.0 .....	285.8   "
$3\frac{1}{2}$ .....	403 .....	25.8 .....	279.0   "
4 .....	403 .....	26.0 .....	279.0   "

The pressure curve (Fig. 1, Curve 1) is very regular, and shows a slight falling off in the rate of change towards the end of the experiment.

The liquid in the worm, which was distinctly acid, contained much formaldehyde, but it did not give the iodoform reaction, nor did it produce a precipitate with a neutral solution of magnesium chloride. It therefore contained neither acetaldehyde nor ethylene oxide. The entire absence of glyoxal was proved by the character of the *p*-bromophenylhydrazone prepared from the liquid, which was identical with that prepared from a dilute solution of formaldehyde. On slowly evaporating the liquid to dryness, there remained only a faint greasy film.

The gaseous products had the following percentage composition:

$$\begin{aligned} \text{CO}_2 &= 35.35; \text{CO} = 21.25; \text{O}_2 = \text{nil}; \text{C}_2\text{H}_4 = 37.10; \text{C}_2\text{H}_6 = 0.30; \\ \text{H}_2 &= 6.00. \end{aligned}$$

The partial pressures of ethylene and oxygen in the original mixture, and of the various gaseous products, were as follows:

#### *Original Mixture.*

Ethylene .....	226.0 mm.	Oxygen .....	228.0 mm.
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#### *Products.*

Carbon dioxide .....	95.6 mm.	Ethylene .....	100.4 mm.
Carbon monoxide ...	57.5 ,,	Ethane .....	0.8 ,,
		Hydrogen .....	16.2 ,,

We see, therefore, that although 124.8 mm. of ethylene were burnt during the experiment, the total quantity of the oxides of carbon in the products only amounted to 153.1 mm. Assuming that 16.2 mm. each of hydrogen and carbon monoxide had been formed by the thermal decomposition of formaldehyde, we calculate that 47.8 mm. of ethylene had been completely burnt to carbon dioxide and steam, and 20.7 mm. to carbon monoxide and steam. This would account for 68.5 mm. of ethylene and 184.9 mm. of oxygen. There would thus remain no less than 56.4 mm. of ethylene, or about 45 per cent. of the total quantity burnt, and 43.1 mm. of oxygen to be accounted for as formaldehyde, and possibly also as some less oxygenated soluble intermediate product.

#### *3rd Experiment.*

In this experiment we used a mixture approximating in composition to  $3\text{C}_2\text{H}_4 + 2\text{O}_2$ ; it contained 60.7 and 39.3 per cent. of ethylene and

oxygen respectively. The oxidation extended over 3 days, the temperature of the combustion tube being allowed to rise slowly from 330° to 390° as the process went on.

Pressure of the cold dry nitrogen-free

original mixture at 18° ..... = 492.7 mm.

Pressure of the cold dry nitrogen-free

final products at 18° ..... = 335.5 mm.

Fall = 157.2 mm., or 31.9 per cent.

The liquid in the worm at the end of the experiment had a neutral reaction; it contained much formaldehyde, but neither acetaldehyde nor ethylene oxide. The gaseous products, which still contained a little oxygen, had the following percentage composition:

$\text{CO}_2 = 28.4$ ;  $\text{CO} = 6.4$ ;  $\text{O}_2 = 1.5$ ;  $\text{C}_2\text{H}_4 = 62.2$ ;  $\text{C}_2\text{H}_6 = 0.6$ ;  $\text{H}_2 = 0.9$ .

Comparing again the partial pressures of the ethylene and oxygen in the original mixture with those of the gaseous products, we obtain the following numbers:

*Original Mixture.*

Ethylene..... 299.2 mm.      Oxygen..... 193.5 mm.

*Products.*

Carbon dioxide... 95.3 mm.	Ethylene ..... 208.8 mm.
Carbon monoxide 21.4 „	Ethane..... 2.0 „
Oxygen ..... 5.0 „	Hydrogen ..... 3.0 „

The pressure of the ethylene burnt was therefore  $299.2 - 208.8 - 2.0$ , or 88.4 mm., whilst the total pressure of the oxides of carbon in the products was only 116.7 mm. Assuming again that the 3.0 mm. of hydrogen and 2.0 mm. of ethane had been produced by the secondary decompositions of formaldehyde,  $\text{CH}_2\text{O} = \text{CO} + \text{H}_2$  and  $\text{CH}_2\text{O} + \text{C}_2\text{H}_4 = \text{CO} + \text{C}_2\text{H}_6$ , we calculate that 47.65 mm. of ethylene had been burnt to carbon dioxide and steam, 8.2 mm. to carbon monoxide and steam, and the remaining 32.55 to formaldehyde. This conclusion agrees fairly well with the amount of oxygen which disappeared during the experiment, namely 188.5 mm., thus:

47.65	C <sub>2</sub> H <sub>4</sub>	burnt to	2CO <sub>2</sub> + 2H <sub>2</sub> O	would require	142.95 mm. O <sub>2</sub> .
8.2	„	„	2CO + 2H <sub>2</sub> O	„	16.40 „
32.55	„	„	2CH <sub>2</sub> O	„	32.55 „

Total = 191.90

*Ath Experiment.*

In this experiment the combustion took place at a considerably higher temperature, and, in consequence, the process was greatly accelerated, the whole of the oxygen disappearing within about 6 hours. The very rapid oxidation had a marked effect on the quantity of formaldehyde which escaped further oxidation, much less of this product being absorbed by the liquid in the worm than in the previous experiments. The mixture used contained 49.1 and 50.9 per cent. of ethylene and oxygen respectively.

Pressure of the dry "nitrogen-free"

original mixture at 20° ..... = 449.2 mm.

Pressure of the dry "nitrogen-free"

final products at 20° ..... = 301.5 mm.

—————  
Fall = 147.7 mm., or 32.9 per cent.

Records were taken every two hours during the experiment, as follows:

Hour.	<i>T.</i>	<i>t.</i>	<i>P.</i>
0 .....	470° .....	20.5° .....	461.4 mm.
2 .....	501 .....	25.0 .....	385.0 „
4 .....	503 .....	26.5 .....	332.7 „
6 .....	502 .....	28.0 .....	320.4 „
8 .....	501 .....	29.0 .....	318.0 „
10 .....	502 .....	29.0 .....	318.0 „

The pressure curve, which is of a similar type to those obtained in the previous experiments, is shown in Fig. 2 (p. 1662).

The liquid in the worm was distinctly acid, and contained traces of formaldehyde, but did not give the iodoform reaction.

The gaseous products had the following percentage composition:

$\text{CO}_2 = 43.2$ ;  $\text{CO} = 7.6$ ;  $\text{C}_2\text{H}_4 = 44.8$ ;  $\text{C}_2\text{H}_6 = 0.4$ ;  $\text{H}_2 = 4.0$ .

The partial pressures of ethylene and oxygen in the original mixture and of the various gaseous products are shown below:

*Original Mixture.*

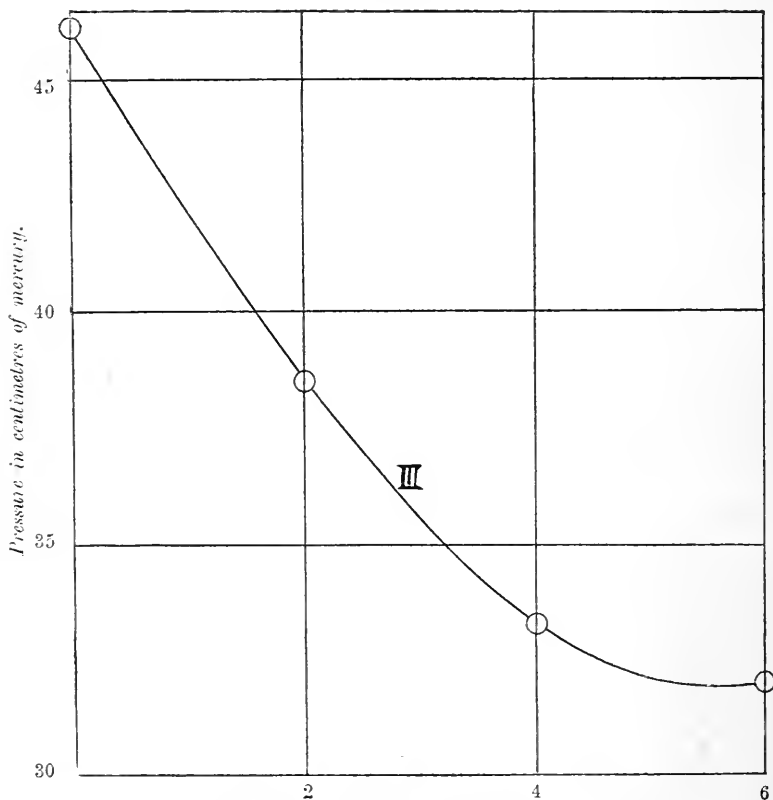
Ethylene..... 220.5 mm.      Oxygen..... 228.7 mm.

*Products.*

Carbon dioxide...	130.5 mm.	Ethylene .....	135.0 mm.
Carbon monoxide	23.0 „	Ethane.....	1.0 „
		Hydrogen .....	12.0 „

Assuming, as before, that the ethane and hydrogen were formed by the secondary decompositions of formaldehyde, we calculate that, of the 84.2 mm. of ethylene burnt, 65.25 were accounted for in the products as carbon dioxide and steam, and 5 mm. as carbon monoxide and steam. This would leave 13.95 mm. of ethylene and 23.08 mm. of oxygen to be accounted for as formaldehyde or its decomposition

FIG. 2.

*Curve III. Time periods in hours.*

products, and possibly also some more highly oxygenated intermediate product.

In addition to the experiments just described, we made five others with the circulation apparatus under varying conditions, without gaining any further information as to the course of the combustion. In two of these experiments the worm of the apparatus contained a neutral solution of magnesium chloride; the liquid, however, remained

clear up to the end of each experiment, a circumstance which indicates the absence of ethylene oxide. In none of the five experiments was there any evidence of the formation of acetaldehyde. We therefore conclude that under the conditions of the circulation experiments the whole of the vinyl alcohol, which was probably the primary oxidation product, was very rapidly further oxidised to formaldehyde through the unstable dihydroxyethylene. The composition of the gaseous products always harmonised with this assumption.

In conclusion, we have much pleasure in again thanking the Government Grant Committee of the Royal Society for the continuance of grants towards the expenses of this and cognate researches.

THE UNIVERSITY,  
MANCHESTER.

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CLXVI.—*Isomeric Change of Diacylanilides into Acylaminoketones. Transformation of Dibenzoylamino-benzophenone into 1-Benzoylamino-2 : 4-dibenzoylbenzene.*

By FREDERICK DANIEL CHATTAWAY and WILLIAM HENRY LEWIS.

In the intramolecular rearrangements occurring among derivatives of aromatic amines, in which aminic hydrogen is replaced by various atoms or groups which subsequently change places with the hydrogen atoms of the nucleus, the isomeric changes occur progressively until the para- and both ortho-positions are occupied by substituting groups. This is well seen in those cases where alkyl groups or halogen atoms are concerned.

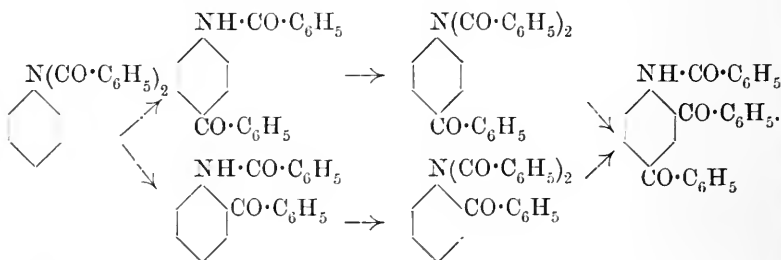
It has recently been shown (Chattaway, this vol., p. 386; Chattaway and Lewis, this vol., p. 499) that diacyl derivatives of aromatic amines can undergo similar isomeric changes; the benzoyl group, for example, leaving the nitrogen and entering either an ortho- or the para-position in aniline and the toluidines.

If the transformation of diacylanilides is strictly analogous to other intramolecular rearrangements of this type, the diacyl derivatives of *o*- and *p*-aminoketones under the influence of a suitable catalyst should themselves undergo transformation into an isomeride containing two acyl groups in positions 2 and 4 relatively to the nitrogen, this being the chief product of the isomeric change either of an ortho- or of a para-

compound. The ease with which such a substance would be decomposed precludes, however, the possibility of the yield being large.

In order to determine whether the transformation of diacylamino-derivatives can progress beyond the first stage so that two groups enter the ring, a careful examination has been made of the product obtained by heating dibenzanilide with excess of benzoyl chloride, this, owing to the comparative readiness with which the first transformation takes place, being equivalent to heating dibenzoylaminobenzophenone in the presence of hydrogen chloride. From the product, after hydrolysis, aminodibenzoylbenzene has been isolated.

As both *o*- and *p*-benzoylaminobenzophenones are initially formed, there seems little doubt that this base is 1-amino-2:4-dibenzoylbenzene and that the transference of acyl groups into the ring follows a precisely similar course to that taken in the intramolecular rearrangements in which alkyl groups or halogen atoms are introduced, thus :



*Transformation of Dibenzoyl-*o*- and -*p*-aminobenzophenones into 1-Benzoylamino-2:4-dibenzoylbenzene.*

It having been shown (*loc. cit.*) that benzoyl-*o*- and -*p*-aminobenzophenones are produced in the transformation of dibenzanilide, these compounds were not isolated, but the successive actions were carried out in one operation. The equivalent quantity of benzoyl chloride (3 molecules) was added to aniline (1 molecule) and the whole was heated in an oil-bath. An interaction occurred and the temperature was gradually raised until it reached 220—230°, at which point it was maintained for 40—50 hours. The viscid, tarry mass thus produced was dissolved in a large excess of alcohol containing about one-third of its volume of strong hydrochloric acid and the liquid boiled for about 16 hours to hydrolyse completely all benzoyl derivatives. Steam was then blown through the liquid to expel the alcohol and the ethyl benzoate formed. When these had been driven off, the residue was made alkaline and steam again passed in order to remove any aniline or unchanged *o*-aminobenzophenone. The tarry residue in the distilling flask was next washed several times with hot water to remove most of the unchanged *p*-aminobenzophenone. The portion

undissolved by the water was then extracted with moderately strong warm hydrochloric acid, and from this extract, on adding caustic soda, a yellow or brown basic solid was deposited. This was dissolved in alcohol, boiled with animal charcoal to remove some of the colour, and the product which separated on cooling was subjected to a prolonged fractional crystallisation from alcohol and from chloroform. The substance finally obtained gave on combustion numbers corresponding with the composition of aminodibenzoylbenzene. It is very difficult to burn the compound completely.

0.4300 gave 1.2567  $\text{CO}_2$  and 0.1951  $\text{H}_2\text{O}$ .  $\text{C} = 79.71$ ;  $\text{H} = 5.08$ .

0.2774 „ 11.15 c.c. of nitrogen at  $19^\circ$  and 762 mm.  $\text{N} = 4.73$ .

$\text{C}_{20}\text{H}_{15}\text{O}_2\text{N}$  requires  $\text{C} = 79.69$ ;  $\text{H} = 5.02$ ;  $\text{N} = 4.66$  per cent.

For the reasons stated above, the compound is probably 1-amino-2:4-dibenzoylbenzene; it is easily soluble in alcohol or chloroform and crystallises in clusters of short, rectangular, pale yellow plates (m. p.  $138^\circ$ ). It yields an acetyl and a benzoyl derivative and dissolves in moderately strong acids, giving a clear solution from which the base is reprecipitated on the addition of much water.

*1-Acetylamino-2:4-dibenzoylbenzene*,  $\text{C}_6\text{H}_3(\text{NH}\cdot\text{CO}\cdot\text{CH}_3)(\text{CO}\cdot\text{C}_6\text{H}_5)_2$ .—This compound, which is readily formed by warming the base with the equivalent quantity of acetic anhydride for a short time on the water-bath, is easily soluble in alcohol and chloroform; it crystallises in clusters of short, six-sided, very pale yellow plates (m. p.  $131^\circ$ ).

0.3130 gave 0.8822  $\text{CO}_2$  and 0.1436  $\text{H}_2\text{O}$ .  $\text{C} = 76.87$ ;  $\text{H} = 5.13$ .

$\text{C}_{22}\text{H}_{17}\text{O}_3\text{N}$  requires  $\text{C} = 76.93$ ;  $\text{H} = 4.99$  per cent.

*1-Benzoylamino-2:4-dibenzoylbenzene*,



This compound is produced when the base is mixed with the equivalent quantity of benzoyl chloride and the mixture heated on the water-bath, at first alone and afterwards with a dilute solution of potassium hydrogen carbonate. It crystallises from alcohol in small, colourless, pearly plates (m. p.  $156^\circ$ ).

0.2588 gave 0.7613  $\text{CO}_2$  and 0.1160  $\text{H}_2\text{O}$ .  $\text{C} = 80.23$ ;  $\text{H} = 5.02$ .

0.3038 „ 9.1 c.c. nitrogen at  $16^\circ$  and 770 mm.  $\text{N} = 3.60$ .

$\text{C}_{27}\text{H}_{19}\text{O}_2\text{N}$  requires  $\text{C} = 79.96$ ;  $\text{H} = 4.73$ ;  $\text{N} = 3.46$  per cent.

The yield of 1-amino-2:4-dibenzoylbenzene is so small, not more than 2 to 3 per cent. of the weight of aniline used, and its isolation so tedious that sufficient has not been obtained to make a more extended study of its behaviour.

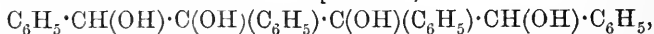
CLXVII.—*The Grignard Reaction applied to the Esters of Hydroxy-acids.*

By PERCY FARADAY FRANKLAND and DOUGLAS FRANK TWISS, M.Sc.

For some time past we have been engaged in studying the behaviour of the esters of hydroxy-acids towards magnesium alkyl and aryl haloids, and the recent appearance of a paper by S. F. Acree\* in which the action of magnesium phenyl bromide on methyl mandelate with production of triphenylglycol,  $(C_6H_5)_2C(OH) \cdot CH(OH) \cdot C_6H_5$ , is incidentally described, leads us to communicate without further delay some results we have obtained in this investigation, which is still in progress.

By the action of magnesium phenyl bromide on dimethyl tartrate we have obtained a tetraphenylerythritol, presumably the *aaδδ*-compound,  $(C_6H_5)_2C(OH) \cdot CH(OH) \cdot CH(OH) \cdot C(OH)(C_6H_5)_2$ , as a colourless, crystalline substance, melting at  $148^\circ$  and exhibiting a very high dextrorotation. In ethyl-alcoholic solution (4.327 per cent.),  $[\alpha]_D^{20} + 182.8^\circ$ .

It is thus isomeric with benzoïnpinacone,



obtained by the electrolytic reduction of benzil or benzoïn, which melts at  $235^\circ$  and is, of course, inactive (Kauffmann, *Chem. Centr.*, 1898, i, 1232).

*Action of Magnesium Phenyl Bromide on Dimethyl Tartrate.*—Twenty-five grams of cleaned magnesium were added to 160 grams of bromobenzene dissolved in 350 grams of dry ether. A trace of iodine was added to start the reaction, after which the latter had to be moderated by cooling the liquid. When the action was complete, the liquid was cooled in ice and 20 grams of methyl tartrate dissolved in 150 c.c. of dry ether were added. The action was at first very slow, a white solid separating in lumps, but on removing the flask from the ice the liquid began to boil vigorously, and cooling had again to be resorted to. Subsequently the flask was cautiously warmed and finally heated for 6—8 hours on the boiling water-bath, a viscid, light brown liquid separating out on the bottom. When cold, the contents of the flask were poured into water and acidified with sulphuric acid. The ethereal layer was separated, and the aqueous part further extracted two or three times with ether. The ethereal solution was dried with anhydrous sodium sulphate, and, after evaporating off the ether, a viscid,

\* "On some Syntheses with the Aid of Sodium Phenyl and Alkyl Magnesium Bromides," *Ber.*, 1904, 37, 2753.

yellow liquid remained, which became solid in the steam-oven. The solid was crystallised from 50 per cent. alcohol. The alcoholic solution was optically active, and the substance was therefore recrystallised until of constant rotation. It forms small, white needles practically insoluble in water and melting at  $148^{\circ}$ .

I. 0.1890 gave 0.5456  $\text{CO}_2$  and 0.1094  $\text{H}_2\text{O}$ .  $\text{C} = 78.73$ ;  $\text{H} = 6.43$ .

II. 0.1918 „ 0.5522  $\text{CO}_2$  and 0.1062  $\text{H}_2\text{O}$ .  $\text{C} = 78.52$ ;  $\text{H} = 6.15$ .

Tetraphenylerythritol,  $\text{C}_{28}\text{H}_{26}\text{O}_4$ , requires  $\text{C} = 78.87$ ;  $\text{H} = 6.10$  per cent.

The following rotations in ethyl-alcoholic solution were obtained :

<i>p.</i>	<i>d</i> $20^{\circ}/4^{\circ}$ .	<i>l.</i>	$\alpha_D^{20^{\circ}}$ .	$[\alpha]_D^{20^{\circ}}$ .	$[\text{M}]_D^{20^{\circ}}$ .
4.327	0.8037	0.999	+6.35°	+182.8°	+779°
1.537	0.7947	3.899	+8.63	+181.1	+771

The molecular weight was determined by the cryoscopic method in benzene solution :

Grams substance per 100 grams solvent.	$\Delta$ .	Molecular weight (molecular depression for benzene = 49).
1.051	0.102°	504.9
3.078	0.260	580.0
5.804	0.445	639.2

Normal molecular weight,  $\text{C}_{28}\text{H}_{26}\text{O}_4 = 426$ .

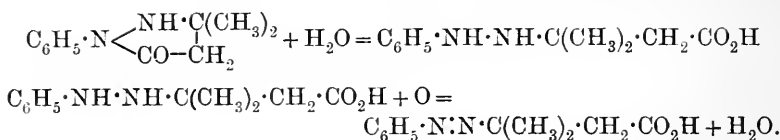
Tetraphenylerythritol is thus considerably associated even in a 1 per cent. solution of benzene.

THE UNIVERSITY,  
BIRMINGHAM.

### CLXVIII.—*The Constitution of Pyrazolidone Derivatives: $\beta$ -Phenylazoisovaleric Acid and s- $\beta$ -Phenylhydrazinobutyric Acid.*

By BERTRAM PRENTICE.

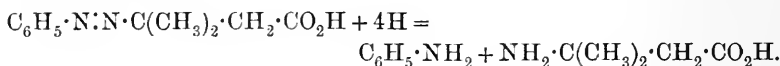
IN describing the preparation of 1-phenyl-3 : 3-dimethyl-5-pyrazolidone by the condensation of dimethylacrylic acid and phenylhydrazine (*Annalen*, 1896, 292, 272), I also showed that this compound, when hydrolysed with barium hydroxide, gave  $\beta$ -phenylazoisovaleric acid, the intermediate product,  $\beta$ -phenylhydrazinoisovaleric acid, being oxidised during the hydrolysis in the following manner :



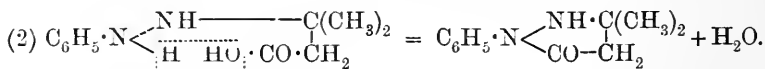
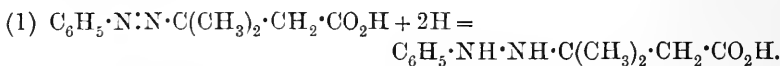
The study of this acid was continued in order to establish its constitution and thus add further proof to the constitution of 1-phenyl-3:3-dimethyl-5-pyrazolidone, from which it was derived.

*Action of Reducing Agents on  $\beta$ -Phenylazoisovaleric Acid.*

The action of various reducing agents on  $\beta$ -phenylazoisovaleric acid was tried with the object of decomposing it into  $\beta$ -aminoisovaleric acid and aniline, thus:



When treated with acid reducing agents, this acid is converted into 1-phenyl-3:3-dimethyl-5-pyrazolidone, being reduced to  $\beta$ -phenylhydrazinoisovaleric acid, which immediately condenses to the inner anhydride:



The reactions involved in the reduction of  $\beta$ -phenylazoisovaleric acid are thus the reverse of those which occur in its production. The hydrolysis of 1-phenyl-3:3-dimethyl-5-pyrazolidone and its regeneration from the product complete the proof of its constitution. This proof is of especial importance, as this 3:3-disubstituted pyrazolidone cannot be oxidised to a corresponding pyrazolone derivative. The reaction also shows that the formula previously assigned to  $\beta$ -phenylazoisovaleric acid is correct.

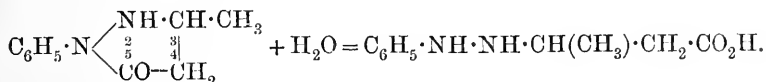
When reduced in acid solution,  $\beta$ -phenylazoisovaleric acid always yields phenyldimethylpyrazolidone, water (1 mol.) being eliminated. Such a condensation could not, however, take place with the sodium salt of the acid, and hence the action of various reducing agents was tried on sodium phenylazoisovalerate in alkaline solution.

Sodium and ethyl alcohol gave only negative results, whereas with sodium and amyl alcohol half the acid was recovered unchanged, the remainder being converted into phenyldimethylpyrazolidone.

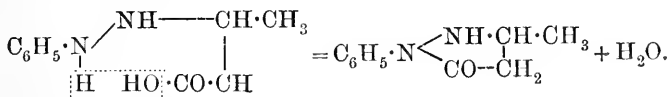
*The Constitution of 1-Phenyl-3-methyl-5-pyrazolidone and s-β-Phenylhydrazinobutyric Acid.*

The interesting result obtained by boiling 1-phenyl-3:3-dimethyl-5-pyrazolidone with barium hydroxide solution led me to investigate the action of this alkali on other pyrazolidones in order to ascertain whether the reaction was a general one.

1-Phenyl-3-methyl-5-pyrazolidone was found to be converted into s-β-phenylhydrazinobutyric acid when boiled with barium hydroxide, a change nearly analogous to the action of this alkali on 1-phenyl-3:3-dimethyl-5-pyrazolidone; the reaction may be represented as follows:



In this instance, the isolation of the β-hydrazino-acid was accomplished; this substance is, however, very unstable, decomposing on exposure to air and being readily converted on heating into phenyl-3-methyl-5-pyrazolidone:



The hydrolysis of 1-phenyl-3-methyl-5-pyrazolidone and its regeneration from the s-β-phenylhydrazinobutyric acid thus produced establish its constitution.

The further investigation of the action of barium hydroxide on pyrazolidones and analogous compounds and the formation of mixed azo- and hydrazino-compounds is in progress.

#### EXPERIMENTAL.

*Reduction of Phenylazoisovaleric Acid.*

Five grams of β-phenylazoisovaleric acid, dissolved in strong hydrochloric acid, were treated with a solution of stannous chloride (1 part) in hydrochloric acid (20 parts) until the yellow colour of the solution had nearly disappeared; the solution was heated for half an hour on the water-bath to complete the reaction, then diluted with water, cooled, and an excess of potassium hydroxide solution added. The tin hydroxide first precipitated was redissolved in excess of the alkali, leaving a permanent sticky, colourless mass which was found to be soluble in ether. The ethereal solution was dried over anhydrous sodium sulphate, filtered, and the ether removed by

distillation. The residue (4.5 grams) was a colourless oil which, on cooling, immediately crystallised in beautiful, radiating groups of colourless needles; when crystallised from light petroleum, it was obtained in the form of long, colourless needles melting at 74—75°. It is easily soluble in alcohol, ether, chloroform, and ligroin, dissolving more sparingly in light petroleum, from which it can be conveniently crystallised.

0.1382 gave 0.3523 CO<sub>2</sub> and 0.099 H<sub>2</sub>O. C = 69.52; H = 7.55.

0.1599 „ 22 c.c. nitrogen at 16° and 745 mm. N = 14.99.

C<sub>11</sub>H<sub>11</sub>ON<sub>2</sub> requires C = 69.47; H = 7.37; N = 14.73 per cent.

The product is therefore 1-phenyl-3:3-dimethyl-5-pyrazolidone, which melts at 74—75° and has all the foregoing properties. Its formation is represented on p. 1668. It is also produced by reducing  $\beta$ -phenylazoisovaleric acid either with tin or zinc in the presence of hydrochloric acid.

*Action of Barium Hydroxide on 1-Phenyl-3-methyl-5-pyrazolidone.*

1-Phenyl-3-methyl-5-pyrazolidone was prepared according to Knorr and Duden's method (*Ber.*, 1893, 26, 103), 24 grams of crotonic acid (1 mol.) and 30 grams of phenylhydrazine (1 mol.) being heated in a small flask at 125° for about 20 minutes. Towards the end of the reaction, the temperature was raised to 165°, and maintained at this point until a portion of the fusion became completely solid when cooled and rubbed with a glass rod. The product was purified by recrystallisation from alcohol and subsequent washing with light petroleum; it crystallises in fine, colourless needles melting at 84—85°. It was identified by the following properties. It is not acidic like the pyrazolones, but is, on the contrary, a weak base; it is not volatile in steam and is precipitated from its cold aqueous solution by sodium hydroxide. Phenylmethylpyrazolidone reduces ammoniacal silver nitrate and Fehling's solution; mercuric oxide and ferric chloride oxidise it to 1-phenyl-3-methyl-5-pyrazolone. When pure 1-phenyl-3-methyl-5-pyrazolidone was boiled with excess of barium hydroxide solution, the substance melted and finally dissolved completely. The colourless solution thus obtained was cooled and extracted with ether; the ethereal extract gave only a trace of residue on evaporation, showing that the basic pyrazolidone had practically all been converted into an acid substance. The liquid was now acidified with dilute sulphuric acid and again extracted with ether; the dry ethereal residue, a viscid, yellow oil, slowly decomposed when left over sulphuric acid in a desiccator and finally changed into a dark brown, sticky mass, from which crystalline substances could not be obtained.

*Preparation of s-β-Phenylhydrazinobutyric Acid.*

A second quantity of 1-phenyl-3-methyl-5-pyrazolidone (5 grams) was boiled with crystallised barium hydroxide (11 grams) and 100 c.c. of water in a reflux apparatus until all the pyrazolidone derivative had passed into solution; the liquid was then cooled, diluted with water, and treated with the calculated quantity of normal sulphuric acid required to precipitate all the barium as sulphate. The mixture was immediately extracted with ether, the ethereal extract thoroughly dried over anhydrous sodium sulphate, filtered, and distilled on a water-bath. The dry residue, weighing rather more than 5 grams, was redissolved in a little dry ether and placed over sulphuric acid in a desiccator, from which the air was immediately expelled by carbon dioxide. When left overnight, a pale yellow, incrustated mass was obtained; this substance was triturated with light petroleum, the residue filtered off, repeatedly washed with the same solvent, and transferred to a desiccator in an atmosphere of carbon dioxide.

s-β-Phenylhydrazinobutyric acid was purified by dissolving it in boiling benzene, from which it crystallises in fine, colourless needles or granules, which melt at 96—97°; it is very soluble in alcohol, ether, glacial acetic acid, or ethyl acetate; it dissolves in chloroform or benzene and can be crystallised from the latter. It is insoluble in ligroin, melts in hot water, and a portion solidifies on cooling; it is mainly decomposed when left in contact with this solvent. The substance is an acid and also a strong reducing agent, interacting with ammoniacal silver nitrate and Fehling's solution even in the cold, and with ferric chloride on warming.

0.1506 gave 0.102 H<sub>2</sub>O and 0.3434 CO<sub>2</sub>. C = 62.18; H = 7.52.

0.1336 „ 0.0892 H<sub>2</sub>O „ 0.3037 CO<sub>2</sub>. C = 61.99; H = 7.41.

0.1799 „ 23.2 c.c. of nitrogen at 18° and 740 mm. N = 14.55.

C<sub>10</sub>H<sub>14</sub>O<sub>2</sub>N<sub>2</sub> requires C = 61.85; H = 7.22; N = 14.43 per cent.

Phenylmethylpyrazolidone (C<sub>10</sub>H<sub>12</sub>ON<sub>2</sub>) contains C = 68.18; H = 6.81; N = 15.9 per cent., whilst the numbers for β-phenylazobutyric acid (C<sub>10</sub>H<sub>12</sub>O<sub>2</sub>N<sub>2</sub>) are C = 62.5; H = 6.25; N = 14.58 per cent.

0.8252 gram of the acid, when titrated with standard potassium hydroxide (1 c.c. = 0.005615 gram KOH), was found to require 42.5 c.c. for exact neutralisation, this corresponding with 0.2387 gram KOH, instead of 0.2377 gram, the amount theoretically required. The new acid is therefore monobasic.

The properties of this acid, especially its liability to direct oxidation in air, its strong reducing action on various substances, and the analytical numbers all indicate that the acid is not β phenylazobutyric

acid and point to its being *s*- $\beta$ -phenylhydrazinobutyric acid produced in the manner represented on p. 1669.

Potassium *s*- $\beta$ -phenylhydrazinobutyrate in neutral solution gave the following reactions: with calcium chloride and lead acetate, no precipitates; with barium chloride, a slightly yellow precipitate; with zinc sulphate, a yellow precipitate which decomposes and becomes oily on boiling; with copper sulphate, a light green precipitate which decomposes on heating; with copper sulphate and sodium hydroxide, a red precipitate of cuprous oxide; with silver nitrate, a yellow precipitate which blackens immediately on exposure to air, or on warming, silver being deposited; ferric chloride yields a light yellow precipitate which gradually becomes darker and darkens rapidly on boiling.

Potassium *s*- $\beta$ -phenylhydrazinobutyrate is obtained in long, very deliquescent plates and needles on evaporating its solution nearly to dryness.

*Regeneration of 1-Phenyl-3-methyl-5-pyrazolidone from s- $\beta$ -Phenylhydrazinobutyric Acid.*

*s*- $\beta$ -Phenylhydrazinobutyric acid, when heated, gradually softens and finally melts with decomposition at 96–97°. Two grams were heated in an oil-bath at 120° for some time, water was evolved, the temperature was raised to 160°, and the heating continued until a small portion of the liquid became completely solid on cooling and rubbing with a glass rod. The pale yellow product was recrystallised from 95 per cent. alcohol and obtained in long, branching needles. It was further purified from any traces of acid impurity by trituration with potassium hydroxide solution, in which it is insoluble, dried on a porous plate, and when recrystallised from diluted alcohol it separates in colourless needles.

The substance, when dried over sulphuric acid in a desiccator, was found to melt at 84–85°; it is easily soluble in alcohol, chloroform, toluene, or glacial acetic acid; it dissolves in ether and in boiling water, and is insoluble in cold aqueous alkalis. It reduces Fehling's solution and ammoniacal silver nitrate.

0.1201 gave 0.0770 H<sub>2</sub>O and 0.3006 CO<sub>2</sub>. C = 68.26; H = 7.12.

0.1563 „ 21.7 c.c. nitrogen at 16° and 756 mm. N = 16.10.

C<sub>10</sub>H<sub>12</sub>ON<sub>2</sub> requires C = 68.18; H = 6.81; N = 15.9 per cent.

The foregoing properties and the analytical data prove that the product is 1-phenyl-3-methyl-5-pyrazolidone, which has thus been regenerated from *s*- $\beta$ -phenylhydrazinobutyric acid.

CLXIX.—*The Acylation of Amides.*

By ARTHUR WALSH TITHERLEY.

It is well known that secondary amides of the type  $\text{RCO}\cdot\text{NH}\cdot\text{COR}$  cannot in general be obtained by introducing an acyl group into primary amides on simple treatment with acyl chlorides. For although diacetamide may be obtained from acetyl chloride and acetamide (Trans., 1901, 79, 411), no interaction takes place between acetyl or benzoyl chloride and benzamide, whilst acetonitrile and benzoic anhydride are produced from benzoyl chloride and acetamide, but no acetylbenzamide (*loc. cit.*; Pinner, *Ber.*, 1892, 25, 1435). By allowing acyl chlorides to act on sodium acylamides,  $\text{R}\cdot\text{CO}\cdot\text{NHNa}$ , a more general reaction is possible, and, as already shown (Trans., 1901, 79, 395), secondary amides readily result, for example :



This process of acylation, however, is limited in its application. Thus the condensation of acetyl chloride with sodium benzamide gave a different result from that of benzoyl chloride with sodium acetamide; the former pair reacted normally, producing acetylbenzamide,

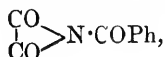


whilst the latter gave a variety of products such as diacetamide, benzonitrile, benzoic anhydride, and tribenzamide.

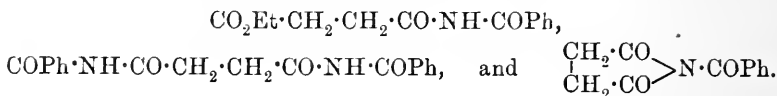
Another method of acylation (Trans., 1902, 81, 1520) is that based on a general reversible change, which occurs when sodium acylamides are heated with esters of monobasic acids, and which is represented approximately by the system  $\text{RCO}\cdot\text{NHNa} + \text{R}'\text{CO}_2\text{Et} \rightleftharpoons \text{RCO}\cdot\text{NNa}\cdot\text{COR}' + \text{EtOH}$ .

The method may be adapted to the synthesis of mixed secondary amides and is fairly easy to carry out, although, as previously shown, it breaks down when esters and sodamide derivatives of fatty acids are employed. In the present investigation, further experiments have been made in order to ascertain whether the esters of oxalic and succinic acids behave like those of monobasic acids. Assuming the above general reaction to hold good, methyl oxalate might be expected to give with sodium benzamide any of the following products :

$\text{CO}_2\text{Me}\cdot\text{CO}\cdot\text{NH}\cdot\text{COPh}$ ,  $\text{COPh}\cdot\text{NH}\cdot\text{CO}\cdot\text{CO}\cdot\text{NH}\cdot\text{COPh}$ , and

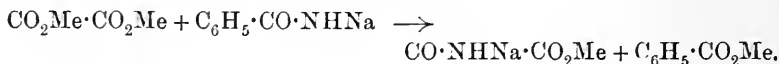


and, similarly, ethyl succinate might yield

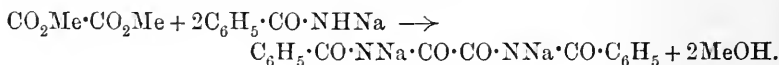


As apparently no acylated derivatives of oxamic acid, oxamide, succinamic acid, and succinamide have hitherto been isolated, it appeared desirable to study further the ester-sodium acylamide method in reference to the synthesis of such compounds, and especial efforts have been made to isolate benzoyloxalimide and benzoylsuccinimide, but in the former case as yet without success.

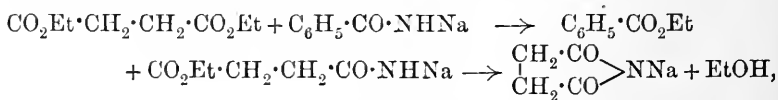
In the action between methyl oxalate and sodium benzamide essentially two changes occur; one leads to the formation of methyl benzoate and probably also sodium methyl oxamate, but owing to its instability the latter could not be isolated:



The other change is normal, yielding disodium dibenzoyloxamide with the liberation of methyl alcohol, thus:



There was no evidence that benzoyloxalimide or methyl benzoyloxamate was produced under any of the different conditions employed in the condensation. Between ethyl succinate and sodium benzamide, condensation takes place at temperatures above  $90^\circ$ , but in accordance with what has already been observed (*loc. cit.*) in reference to the action of esters containing the group  $-\text{CH}_2\cdot\text{CO}_2\text{R}$ , the reaction is abnormal. Neither dibenzoylsuccinamide nor benzoylsuccinimide is produced, although both have been obtained by another process (pp. 1685, 1690), nor is ethyl benzoylsuccinamate formed. The essential change which occurs may be thus represented:



but further complications arise through the interaction of the products with the formation of large quantities of sodium dibenzamide, and sodium benzoate and sodium succinate. It is evident that normal condensations need not be anticipated between the groups  $-\text{CH}_2\cdot\text{CO}_2\text{Et}$  and  $-\text{CO}\cdot\text{NHNa}$ .

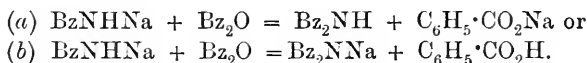
*Acylation by means of Anhydrides.*—Pinner (*Ber.*, 1892, 25, 1434) made several attempts to acylate amides directly by the Schotten-

Baumann and other methods, but without success. He showed that acetylbenzamide (m. p.  $120^{\circ}$ ) could be obtained by heating benzamide and acetic anhydride for half an hour in a reflux apparatus, but benzonitrile and cyaphenine,  $(C_6H_5CN)_3$ , were also formed. Hentschel (*Ber.*, 1890, 23, 2394) succeeded in acetylating acetamide by boiling with acetic anhydride, and obtained as much as 300 grams of diacetamide from 600 grams of acetamide, and it is well known that other compounds containing the CONH group, like isatin, may be similarly acetylated.

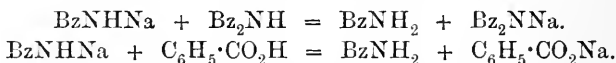
The direct acylation of amides by means of anhydrides is, however, not general, for, whereas it may usually be applied in processes of acetylation with acetic anhydride, it is not applicable in benzoylation, since benzoic anhydride has no action on amides. On this account it is of interest to observe that benzoylation may be effected, at least in the aromatic group, by allowing benzoic anhydride to act on the sodium derivative of an amide. Blacher (*Ber.*, 1895, 28, 2352) first observed the possibility of benzoylation by this method, but made only a few experiments. The change between sodium benzamide (prepared from sodium ethoxide and benzamide) and benzoic anhydride at  $160^{\circ}$  he represented by the equation:  $C_6H_5CONHNa + (C_6H_5CO)_2O = (C_6H_5CO)_2NH + C_6H_5 \cdot CO_2Na$ . Similarly, by the action of acetic anhydride on sodium benzamide, he obtained acetylbenzamide. These observations, however, are incomplete, and only indicate partly what really happens.

When sodium benzamide or other sodium acylamides are prepared by means of sodamide, they react, without the application of heat, on benzoic anhydride with considerable vigour in presence of benzene, and even more energetically in pyridine. The mixture becomes very hot, and viscid, white or grey masses of a gelatinous solid separate consisting chiefly of sodium benzoate and the sodium derivative of the benzoyl compound. The change is not capable of the simple interpretation indicated by Blacher's equation, and usually the benzoylation proceeds further than that corresponding with the introduction of one benzoyl group, so that some of the dibenzoyl derivative appears. Thus, in the action between sodium benzamide and benzoic anhydride in presence of benzene, not only is sodium dibenzamide produced, but also tribenzamide, even when two molecular equivalents of sodium benzamide to one of the anhydride are taken. Moreover, it is found that very little free dibenzamide appears, but large quantities of its sodium derivative and free benzamide are formed during the reaction. These changes have been closely studied with the view of ascertaining whether the interaction of benzoic anhydride and sodium acylamides is of a general character. In the interaction between sodium benzamide and benzoic anhydride, at least two distinct changes must at the

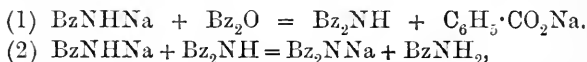
outset occur concurrently, the first leading to the formation of sodium dibenzamide,  $2\text{BzNHNa} + \text{Bz}_2\text{O} = \text{Bz}_2\text{NNa} + \text{BzNH}_2 + \text{C}_6\text{H}_5\cdot\text{CO}_2\text{Na}$ , and the second to that of tribenzamide,  $2\text{BzNHNa} + 2\text{Bz}_2\text{O} = \text{Bz}_3\text{N} + \text{BzNH}_2 + 2\text{C}_6\text{H}_5\cdot\text{CO}_2\text{Na}$ , but these changes may be explained in a different manner. The primary action between sodium benzamide and benzoic anhydride must involve the release of either the sodium or hydrogen atom of the group  $\text{CO}\cdot\text{NHNa}$  (or  $\text{NH}\cdot\text{C}\cdot\text{ONa}$ ) and its combination with the anhydride molecule. Hence, according as the sodium or hydrogen is more mobile, two possibilities are open in this primary action, namely:



Evidence has already been adduced by the author (Trans., 1901, 79, 407) and others as to the superior mobility of the sodium atom in sodium acylamides, and, moreover, there can be no doubt that sodium can be mobile in the present sense, since, as appears on p. 1677, sodium dibenzamide (in which there is no available hydrogen atom) readily reacts with benzoic anhydride in the presence of benzene, forming tribenzamide and sodium benzoate. Of the two alternatives therefore (a) is the more probable, but it is possible that both changes occur simultaneously. In either case, a subsequent secondary change must occur with the formation of free benzamide, for dibenzamide in (a) and benzoic acid in (b), both being much more negative than benzamide, would liberate the latter from its sodium derivative, thus:



Assuming (a) to represent what really takes place, the action of benzoic anhydride on sodium benzamide must then occur in two distinct stages, namely:



or, combining these, we have  $2\text{BzNHNa} + \text{Bz}_2\text{O} = \text{Bz}_2\text{NNa} + \text{BzNH}_2 + \text{C}_6\text{H}_5\cdot\text{CO}_2\text{Na}$ . In accordance with this view, it has been found that the product of the change contains free benzamide, as well as sodium dibenzamide and sodium benzoate.

With respect to the formation of tribenzamide, it is probable that it arises as the product of a secondary change which takes place between a part of the sodium dibenzamide formed in the first stage of the reaction and benzoic anhydride. When the reaction is carried out in presence of pyridine instead of benzene, relatively more tribenzamide is produced and relatively less benzamide recovered. It is very

likely that pyridine, owing to its dissociating and strongly basic character, exerts a determining influence on the course of the reaction and induces the primary change to take place more in the direction of (b) by reason of its affinity for benzoic acid; thus more sodium benzamide would in this case be available for conversion into sodium dibenzamide, part of which would be changed into tribenzamide. Further experiments on the influence of pyridine in these condensations are in progress.

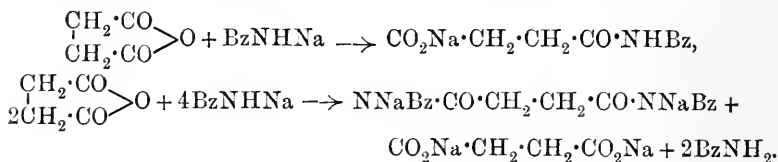
The production of tribenzamide suggested experiments to ascertain whether separately prepared sodium dibenzamide interacts with benzoic anhydride, and it was shown that, even in presence of benzene, they readily yield tribenzamide, thus:  $\text{Bz}_2\text{NNa} + \text{Bz}_2\text{O} \rightarrow \text{Bz}_3\text{N} + \text{C}_6\text{H}_5 \cdot \text{CO}_2\text{Na}$ .

In general, it appears that the anhydride method of acylation applies as well to the sodium derivatives of secondary as to those of primary amides, but the method is not suitable for the benzoylation of sodium acetamide or the acetylation of sodium benzamide. Blacher (*loc. cit.*) has stated that acetic anhydride and sodium benzamide, when heated strongly together, yield acetylbenzamide, but the author has found that when the action is allowed to proceed normally at lower temperatures in presence of benzene very little of the expected acetylbenzamide results, and that the formation of this substance at higher temperatures is to be attributed to the action of the anhydride on free benzamide formed during the reaction (compare Pinner, *loc. cit.*). Large quantities of sodium dibenzamide are produced, and precisely the same kind of action occurs between sodium acetamide and benzoic anhydride. The latter condensation was carried out both in presence of benzene and of pyridine, and although a vigorous action takes place no acetylbenzamide could be isolated from the product, which contained much sodium dibenzamide. These reactions, being of a negative character so far as this work is concerned, were not investigated further, but they appear in both cases to take an abnormal course by reason of the displacement of acetyl by benzoyl, and to conform approximately to the respective equations:



This abnormal behaviour of aliphatic anhydrides and aliphatic sodium acylamides renders it impossible to prepare aliphatic-aromatic mixed secondary amides by this method of acylation. On the other hand, it would appear that cyclic anhydrides react normally. As yet only the condensation of succinic anhydride with sodium benzamide has been studied, the products being the expected benzoylsuccinamic acid and dibenzoylsuccinamide, the synthesis of which was unsuccessfully

attempted in the condensation between ethyl succinate and sodium benzamide. The reactions may be thus represented :

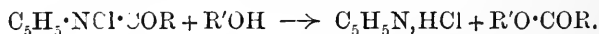


The condensation of maleic, phthalic, and other cyclic anhydrides with sodium benzamide is at present under investigation.

*Acylation of Amides by Acyl Chlorides in the presence of Pyridine.*

The fact that acetamide may be acetylated by means of acetyl chloride whilst benzamide cannot (Trans., 1901, 79, 411), depends probably on the fixation of hydrogen chloride in the former case as acetamide hydrochloride. As the removal of hydrogen chloride appears necessary, pyridine was employed for this purpose and also to promote the acylation of the amides, but while these experiments were being conducted, it was found that Freundler was already engaged in a similar investigation (*Compt. rend.*, 1902, 136, 1553; 1903, 137, 712). He showed that by allowing isobutyryl chloride to fall drop by drop into a pyridine solution of acetamide or acetanilide, the corresponding isobutyryl derivative was formed. He also showed that this method of acylation in presence of pyridine has its limits. Thus, benzoyl chloride acting on acetanilide brings about replacement of acetyl by benzoyl, forming dibenzanilide even when excess of benzoyl chloride is avoided, and, owing to a similar displacement of aliphatic by aromatic acyl groups, acetamide yields, with benzoyl chloride, dibenzamide, an observation which has been confirmed by the author's experiments. On the other hand, the inverse change, that of condensing aliphatic acyl chlorides with aromatic amides, is limited by the fact that these interact with pyridine more or less readily, giving derivatives of dehydracetic acid. Still, by the action of acetyl chloride on benzamide in cold pyridine solution, Freundler obtained some acetylbenzamide.

Dennstedt and Zimmermann have shown that acyl chlorides could act on pyridine, yielding additive compounds, and Minnuni found that the benzoyl derivative,  $\text{C}_5\text{H}_5 \cdot \text{NBzCl}$ , when treated with water gave pyridine hydrochloride and large quantities of benzoic anhydride. The use of pyridine in the acylation of hydroxy-derivatives is well known and has been investigated by Claisen, Einhorn, Kempf, and others, the general mechanism evidently being :



In such processes of acylation, the hydroxyl derivative is usually dissolved in 5—10 times its weight of pyridine, the solution being well cooled and the acyl chloride added gradually. The liquid becomes red, and pyridine hydrochloride usually crystallises out. At the end of 6—8 hours, the product is dropped into cold dilute sulphuric acid in order to precipitate the acyl derivative.

In the benzoylation of amides, the author has employed a somewhat similar process, with results that not only confirm those of Freundler, but which, within the limits previously mentioned, furnish a remarkably easy general method of introducing a benzoyl group into primary or even secondary amides. Thus benzamide gives an almost quantitative yield of dibenzamide, whilst succinimide yields 65 per cent. of benzoyl-succinimide and dibenzamide furnishes 50 per cent. of tribenzamide.

Bearing in view Claisen's striking results in the benzoylation of ethyl acetoacetate in presence of pyridine (*Annalen*, 1896, 291, 25, 106; *Ber.*, 1900, 33, 1242, 3778) whereby he obtained the *o*-benzoyl derivative  $\text{CH}_3\cdot\text{C}(\text{OBz})\cdot\text{CH}\cdot\text{CO}_2\text{Et}$ , it was considered probable that the amides might behave similarly owing to the enolising tendency of the solvent pyridine, and thus yield the imino-ester,  $\text{PhC}(\text{OBz})\cdot\text{NH}$ , from benzamide. Attempts to prove that such imino-esters are produced have been unsuccessful, but it is possible that they are formed as unstable intermediate products which are rapidly transformed into secondary amides. It was found that both acetamide and benzamide yield dibenzamide by the pyridine method of benzoylation, and thus there can be no doubt that benzoyl displaces acetyl. This circumstance indicates the limit to which the method can be applied as a general reaction (compare Freundler, *loc. cit.*).

In short, the methods available for the introduction of an acyl group into a primary or secondary amide are as follows:

(A) Direct action of acyl chloride on amide: a poor method, applicable only to primary amides of the aliphatic series.

(B) Acyl chloride and amide in presence of pyridine: an excellent method for benzoylation, which applies to primary and secondary amides and succinimide, but fails with acetamide, and is not to be recommended for acetylation.

(C) Acyl chloride and sodium acylamides: this process applies in general to acetylation, but to benzoylation in the aromatic group only.

(D) Condensation between esters and sodium acylamides: this method applies to monobasic and dibasic esters (excluding those containing the group  $\text{CH}_2\cdot\text{CO}_2\text{R}$ ) and sodium primary acylamides (excluding those containing the group  $\text{CH}_2\cdot\text{CO}\cdot\text{NHNa}$ ).

(E) Acid anhydride and sodium acylamide: a process applicable for benzoylation in the aromatic group; it applies to sodium derivatives

of primary and secondary amides and to cyclic anhydrides, the reaction being carried out in presence of either benzene or pyridine.

(F) Acid anhydride and amide: this process, which is only applicable for acylation with acetic anhydride and, presumably, its homologues, is not a good method, as the comparatively high temperatures required are apt to produce secondary changes, but the method is valuable as being complementary to E.

In general, it is to be noted that no single method has even approximately the character of a general reaction, but by selecting one of the foregoing processes an acyl group may be introduced into practically any primary or secondary amide or cyclic imide.

#### EXPERIMENTAL.

##### *Action of Methyl Oxalate on Sodium Benzamide.*

Benzamide (24 grams) and sodamide (8 grams) were converted into sodium benzamide (Trans., 1902, 81, 1531), and the latter intimately mixed with methyl oxalate, the mixture being heated in a paraffin-bath, first at 110° for ten minutes, and finally at 120–130° for fifteen minutes, after which the condensation was practically complete. The temperature of the bath was regulated by the rate at which the methyl alcohol formed in the reaction distilled over; 4.8 grams of methyl alcohol were recovered from the distillate, 6.8 grams being the calculated amount according to the equation:



The resulting granular mass was extracted by boiling with twice its weight of a mixture of equal parts of alcohol and benzene and subsequently pure benzene, by which treatment the insoluble *sodium dibenzoyloxamide* was obtained in an impure state as a yellow, gelatinous solid, which became almost white on drying. It was only sparingly soluble in water and was, on digesting with dilute hydrochloric acid, easily converted into dibenzoyloxamide, a thick, white, amorphous solid, which was washed successively with water and boiling alcohol to remove traces of dibenzamide, the yield being 58 per cent. The product was almost entirely soluble in cold dilute sodium hydroxide, and was purified by acidifying the filtered alkaline solution. As the sodium derivative in aqueous solution is very unstable, it was found impossible to purify large quantities in this manner, owing to the delay in filtering, but by working with batches not exceeding 1 gram, and filtering quickly and separately into dilute hydrochloric acid, a considerable quantity was obtained pure.

A careful search failed to reveal the presence of benzoyloxalimide among the products of the reaction, although these contained some

unchanged methyl oxalate and benzamide, together with a considerable quantity (8 grams) of methyl benzoate, formed apparently by a process of double decomposition which has been observed to take place as a secondary change in all sodium acylamide-ester condensations. Oxamide and sodium oxamide were not formed in appreciable quantities.

An alternative treatment to the foregoing, which was adopted in a number of experiments, yielded a second substance, crystallising in plates melting at 158—160° and containing 8·4—8·6 per cent. of nitrogen. This product, which was mistaken at first for benzoyloxalimide, proved to be a molecular compound of benzamide and oxalic acid. It was obtained from the condensation product by treatment with cold dilute hydrochloric acid, and after filtering off the insoluble dibenzoyloxamide it either separated slowly from the filtrate or was extracted with ether. Although insoluble in aqueous alkalis, it was decomposed in the cold even by sodium carbonate, forming sodium oxalate and benzamide.

*s-Dibenzoyloxamide*,  $\text{NHBz}\cdot\text{CO}\cdot\text{CO}\cdot\text{NHBz}$ , melts and decomposes at 227°.

0·1700 gave 0·4028  $\text{CO}_2$  and 0·0653  $\text{H}_2\text{O}$ .  $\text{C} = 64\cdot7$ ;  $\text{H} = 4\cdot27$ .

0·1400 „ 11·3 c.c. moist nitrogen at 17° and 766 mm.  $\text{N} = 9\cdot44$ .

$\text{C}_{16}\text{H}_{12}\text{O}_4\text{N}_2$  requires  $\text{C} = 64\cdot86$ ;  $\text{H} = 4\cdot05$ ;  $\text{N} = 9\cdot46$  per cent.

This substance is a fine white powder, insoluble in all ordinary solvents, but readily soluble in concentrated sulphuric acid, from which, by treating with water, it is precipitated unchanged, and if the sulphuric acid solution is allowed to attract moisture from the air dibenzoyloxamide is deposited in opaque needles. On heating the acid solution, however, it is entirely hydrolysed, and after cooling and diluting pure benzamide crystallises out.

Dibenzoyloxamide readily dissolves in sodium hydroxide, forming its sodium derivative, but the solution on warming breaks down at once into sodium oxalate and benzamide, and even in the cold the hydrolysis is fairly rapid. The benzamide separated as a thick crop of pure crystals melting at 128—129·5°, the yield being nearly theoretical.

It is of interest to note that the products of hydrolysis, however effected, are sodium oxalate and benzamide, and not, as might be anticipated, oxamide and sodium benzoate.

Dibenzoyloxamide forms a *silver* salt, which may be obtained by adding silver nitrate to an aqueous solution of the sodium derivative; it is precipitated as a white, gelatinous solid, and, probably like silver benzamide, contains the grouping  $\text{C}_6\text{H}_5\cdot\text{C}(\text{OAg})\cdot\text{N}\cdot\text{CO}-$  and not  $\text{H}_5\cdot\text{CO}\cdot\text{NAg}\cdot\text{CO}-$ .

*The Molecular Compound,  $2\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{NH}_2, \text{H}_2\text{C}_2\text{O}_4$ .*

The crystals melting at  $158\text{--}160^\circ$ , which were obtained as a by-product in the synthesis of dibenzoyloxamide, were, as previously mentioned, shown to be a molecular compound having the foregoing formula. The compound was purified for analysis by repeated crystallisation from alcohol to remove traces of oxalic acid.

(M. p.  $158^\circ$ ) 0.2678 gave 19.4 c.c. moist nitrogen at  $12^\circ$  and 766 mm.  $\text{N} = 8.66$ .

(M. p.  $160\text{--}161^\circ$ ) 0.2718 gave 19.8 c.c. moist nitrogen at  $9^\circ$  and 773 mm.  $\text{N} = 8.86$ .

$\text{C}_{16}\text{H}_{16}\text{O}_6\text{N}_2$  requires  $\text{N} = 8.43$  per cent.

The molecular character of the substance was apparent from its properties. Moreover, it was found possible to produce it by warming together 4 grams of crystallised oxalic acid and 8 grams of benzamide in 40 c.c. of water. The resulting opaque deposit dissolved on boiling, and on cooling separated to a nearly solid mass of crystals, which, after filtering and drying, melted constantly at  $160^\circ$ , and, on analysis, gave  $\text{N} = 8.50$  per cent.

*Action of Ethyl Succinate on Sodium Benzamide.*

In one series of experiments, 12 grams of benzamide (1 mol.) were added to a solution of 2.3 grams (1 atom) of sodium in 23 grams of alcohol, the alcohol removed at  $120^\circ$ , and the resulting sodium benzamide treated with 17.5 grams of ethyl succinate (1 mol.). The mixture was heated for 20 minutes at  $110\text{--}115^\circ$ , at which temperature a fairly vigorous reaction took place and alcohol distilled over. The residue became liquid and effervesced, and finally separated into two parts. The lower portion was at first a viscous liquid, which solidified on cooling to a brittle glass, and consisted essentially of sodium succinimide; the upper portion, which was oily, contained ethyl benzoate and a little unchanged ethyl succinate. The whole was treated with dilute acetic acid, and after removing the oily upper layer the aqueous solution was concentrated on the water-bath to a syrup, which was then repeatedly extracted with boiling benzene. In this way, succinimide was separated in large quantities and identified by its properties and melting point ( $126^\circ$ ). On fractionation, the oil distilled mainly at  $205\text{--}210^\circ$  and weighed 9.5 grams.

In another series of experiments, benzamide (12 grams) was converted by heating with sodamide (4 grams) into sodium benzamide, which was then heated with ethyl succinate at temperatures ranging

between  $90^{\circ}$  and  $120^{\circ}$ . The same products resulted as in the previous series, but the change was not so complete. Free benzamide (2.53 grams, m. p.  $128^{\circ}$ ) was formed, which was extracted by boiling the product with benzene and filtering hot from the insoluble solid A. Ethyl benzoate was also extracted, 6.5 grams being recovered (b. p.  $205-206^{\circ}$ ). The solid residue A consisted essentially of sodium succinimide and unchanged sodium benzamide, together with sodium succinate, sodium benzoate, and sodium dibenzamide in varying amounts, which increased when higher temperatures were employed in the condensation.

Moreover, three other products were obtained in small quantities. One of these, which melted at  $135^{\circ}$ , formed long prisms, sparingly soluble in water, and dissolved in sodium carbonate, but not in the hydrogen carbonate, being reprecipitated by acids from the alkaline solution as a microcrystalline powder.

0.1220 gave 7.3 c.c. moist nitrogen at  $16^{\circ}$  and 762 mm.  $N = 6.98$  per cent.

Owing to lack of material, this substance has not been identified. As the percentage of nitrogen is the same as that required for benzoylsuccinimide ( $N = 6.9$  per cent.), it was at first supposed to be this substance. Benzoylsuccinimide, however, melts at  $130^{\circ}$  and is quite insoluble in sodium carbonate (see p. 1685).

A second substance obtained in the condensation between ethyl succinate and sodium benzamide (from sodamide) was isolated from the residue A by treatment with caustic soda. A large quantity of insoluble matter remained, chiefly benzamide, containing a very small quantity of a substance melting at  $191^{\circ}$ , isolated by fractional crystallisation from hot water. From boiling alcohol, it is separated as silky needles (m. p.  $192^{\circ}$ ), but the amount obtained from all the experiments was insufficient for analysis.

A third substance was obtained by treating residue A with hydrochloric acid, filtering, and allowing the filtrate to evaporate spontaneously. Transparent plates separated, melting at  $128^{\circ}$ , which were at once rendered opaque by caustic soda or sodium carbonate, and were evidently not benzamide. The substance proved to be a molecular compound, having the formula  $2C_6H_5 \cdot CO \cdot NH_2, C_2H_4(CO_2H)_2$ . The same substance may be readily obtained by dissolving benzamide (2 mols.) and succinic acid (1 mol.) in boiling alcohol and cooling, when it separates in fine, silky needles. Although the best yield is obtained with the foregoing ratio, the same compound results when other proportions are taken. Thus, 5 grams of benzamide (1 mol.) and 5 grams of succinic acid (1 mol.), when dissolved in 40 c.c. of absolute alcohol, yielded on cooling 2 grams of the molecular compound,

more being obtained by boiling the mother liquor with a further quantity of benzamide and allowing the solution to cool. The composition was determined by titration with *N*/10 sodium hydroxide.

First crop, 0.2028 required 11.4 c.c. *N*/10 NaOH. Succinic acid = 33.16 per cent.

Second crop, 0.2051 required 11.48 c.c. *N*/10 NaOH. Succinic acid = 33.01 per cent.

After recrystallisation from hot absolute alcohol, the substance was obtained quite pure in long needles melting at 128.5°.

0.1426 required 7.95 c.c. *N*/10 NaOH. Succinic acid = 32.9 per cent.

$C_{18}H_{20}O_6N_2$  requires succinic acid = 32.77 per cent.

The same compound is produced in large, flat, rectangular prisms when an aqueous solution containing succinic acid and benzamide, and a little alcohol to keep the latter in solution, is slowly allowed to evaporate.

*Action of Benzoyl Chloride on Amides in presence of Pyridine.*

Benzoyl chloride and benzamide in the presence of pyridine interact with considerable evolution of heat, forming dibenzamide and pyridine hydrochloride. Benzamide (1 mol.) dissolved in 5 times its weight of pure pyridine was treated gradually with benzoyl chloride (1 mol.) and the mixture kept cool during the addition. The resulting deep-red solution, which gradually deposited crystals of pyridine hydrochloride, was left in a bath of cold water for 8 hours, after which it was shaken with 3—4 times its volume of water in order to remove the majority of the pyridine. An oil separated, which was extracted with ether and the ethereal solution washed with dilute sulphuric acid to remove the remainder of the pyridine. White needles of dibenzamide (m. p. 144°) separated, which were removed and the ethereal solution evaporated. An oil remained containing benzoic anhydride, a little benzonitrile, but chiefly dibenzamide, which slowly crystallised. Moreover, the aqueous solution obtained by shaking the original product with water slowly deposited dibenzamide in long needles, and the total quantity recovered was equivalent to a nearly theoretical yield as calculated from the equation:  $BzNH_2 + BzCl = Bz_2NH + HCl$ .

Benzoyl chloride and acetamide in the presence of pyridine interact vigorously, but without forming acetylbenzamide. Twelve grams of acetamide (1 mol.) dissolved in 32 grams of pyridine were treated gradually with 28 grams of benzoyl chloride (1 mol.), the mixture being kept cool and left for 12 hours. The whole became red and syrupy, but pyridine hydrochloride, although formed, did not crystallise

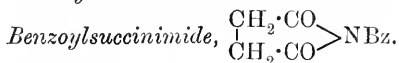
out. The mixture was shaken with ether (about 300 c.c.), the ethereal solution separated from the insoluble syrup, and washed successively with dilute sulphuric acid, water, and sodium carbonate solution, and finally dried over sodium sulphate. On removing the ether, the residual oil was placed in a vacuum. After about a fortnight, needles began to separate, and in two months the residue had about half solidified. The solid, after draining and washing with cold benzene, melted at  $140-144^{\circ}$  and was found to be practically pure dibenzamide. Neither acetylbenzamide nor tribenzamide was present. The liquid portion was a mixture of benzoic anhydride and dibenzamide.

In another experiment, the oil which presented such difficulty in crystallising was quickly fractionated under reduced pressure. The temperature rose steadily from  $110^{\circ}$  to  $220^{\circ}$ , when the distillation was stopped. There was evident decomposition, and an oily distillate came over. The more volatile fractions of this oil consisted of benzonitrile, dibenzamide, and benzoic acid, and the less volatile of benzoic anhydride and tribenzamide (melting at  $40^{\circ}$  and  $203^{\circ}$  respectively). There was no evidence of the presence of ethyl acetiminobenzoate.

*Benzoyl Chloride and Dibenzamide.*

Dibenzamide (1 mol.) dissolved in three times its weight of pyridine, in which it is easily soluble, was treated with benzoyl chloride (1 mol.). The mixture grew warm, and was cooled and left for 8 hours, during which time crystals of pyridine hydrochloride separated and the mixture gradually darkened to a port wine tint. The whole was treated with 8 times its volume of absolute alcohol, which slowly brought down a crystalline precipitate of shining needles, consisting of pure tribenzamide (m. p.  $206^{\circ}$ ). A further crop of impure crystals was obtained by evaporating the mother liquor, and the total yield was 50 per cent. of the theoretical amount.

*Benzoyl Chloride and Succinimide.*



Ten grams of succinimide (1 mol.) dissolved in 20 grams of pyridine were treated gradually with 14 grams of benzoyl chloride (1 mol.), the whole being kept well cooled in a stream of water as considerable heat is developed. The mixture, which became red, was left for about 12 hours, by which time clusters of large crystals of the benzoyl derivative had separated. Eighty c.c. of absolute alcohol were added and the whole shaken, when, after a short time, thick masses of small, white, glistening plates were deposited. The product, which was collected and washed with alcohol, weighed 11.5 grams and consisted of

pure benzoylsuccinimide. A further crop of crystals (1.5 grams) was obtained from the mother liquor on evaporation, the total yield being 65 per cent. of the theoretical amount. The substance crystallised from hot alcohol in very light, pearly-white plates melting at 129–130°.

0.1356 gave 8.32 c.c. moist nitrogen at 22° and 754 mm.  $N = 6.95$ .

$C_{11}H_9O_3N$  requires  $N = 6.90$  per cent.

Benzoylsuccinimide is sparingly soluble in hot water and almost insoluble in cold alcohol and benzene. It is insoluble in cold aqueous caustic soda and sodium carbonate, but is readily hydrolysed by these reagents on warming. When carefully hydrolysed by sodium carbonate and the solution acidified, benzoylsuccinamic acid,



is precipitated in needles melting at 178°. It is identical with the compound obtained by the condensation of succinic anhydride and sodium benzamide.

#### *Condensation of Sodium Acylamides with Anhydrides.*

The sodium acylamide was in all cases obtained by the action of sodamide on the amide by the usual method (*loc. cit.*), and suspended in either benzene or pyridine and treated with the anhydride usually dissolved in the same solvent. Generally a reaction commenced immediately, and was subsequently completed by heating on the water-bath for two to three hours. The separation of the acylated derivative from the product of the reaction was usually comparatively easy.

Acetic anhydride and sodium benzamide react energetically with development of heat, but give only small quantities of acetylbenzamide; 13.6 grams of benzamide and 4.4 grams of sodamide were converted into sodium benzamide (1 mol.) and suspended under 150 c.c. of benzene. A solution of 10.75 grams of freshly distilled acetic anhydride in benzene was added gradually, and the action completed by boiling for several hours. After removing the benzene by distillation, the residual discoloured jelly was treated with cold water and acidified with acetic acid. An oil separated, which slowly solidified to a crystalline mass, which was found to consist of approximately equal parts of benzamide (m. p. 128°) and dibenzamide (m. p. 144°). A little acetylbenzamide (m. p. 117°) was also present, but the amount was too small to be purified. The substance could not be purified by a method similar to that employed in the case of dibenzamide, namely, by solution in sodium hydroxide and reprecipitation with acids, because in aqueous alkaline solution the sodium derivative

is so readily hydrolysed; the liquid set to a crystalline mass in a few minutes, even in the cold, owing to the formation of benzamide. Sodium dibenzamide is much more stable in aqueous solution.

*Benzoic Anhydride and Sodium Acetamide.*

(1) *In presence of Pyridine.*—Six grams of acetamide dissolved in 15 grams of pyridine were converted by means of 4 grams of sodamide into sodium acetamide, and in order to complete the conversion the resulting jelly was heated for an hour in a bath at  $130^{\circ}$  in a reflux apparatus. The product was then cooled and treated gradually with 11.3 grams of benzoic anhydride (that is, 1 mol. anhydride : 2 mols. sodium acetamide) dissolved in 10 grams of pyridine. An energetic reaction set in which was moderated by cooling, and a brown, semi-solid mass resulted. The latter was treated with dilute hydrochloric acid until nearly all the pyridine had been neutralised. An oily precipitate, which slowly solidified, consisted of impure dibenzamide (m. p.  $144^{\circ}$ ) and some benzoic acid. A purer product (m. p.  $146^{\circ}$ ) was slowly deposited from the slightly alkaline filtrate as a mass of needles.

(2) *In presence of Benzene.*—The benzoic anhydride and sodium acetamide interacted much more gently and without darkening, but the result was the same as when pyridine was employed as a menstruum. In both cases, large quantities of sodium dibenzamide were produced, but no acetylbenzamide.

*Benzoic Anhydride and Sodium Benzamide.*

(1) *In presence of Pyridine.*—The preparation of sodium benzamide from benzamide and sodamide is more rapid and sooner completed in presence of pyridine than in that of benzene. Twelve grams of benzamide dissolved in the minimum quantity of pyridine were added slowly to 4 grams of finely powdered sodamide suspended in 10 grams of benzene. The whole grew very hot, ammonia was copiously evolved, and a thick, white magma of sodium benzamide resulted, suspended in a mixture of pyridine and benzene. After completing the conversion by heating, the paste was treated gradually with a solution of 22 grams of benzoic anhydride (1 mol. : 1 mol. sodium benzamide) in 20 grams of pyridine. The mixture grew hot and became nearly solid, but there was no discoloration. After half an hour, it was treated with water containing a little sodium hydroxide. A white solid remained insoluble, which, after washing with hot water and drying, weighed 2.5 grams. It consisted of pure tribenzamide and melted at  $203^{\circ}$ .

0.2280 gave 8.4 c.c. moist nitrogen at 23° and 752 mm.  $N = 4.10$ .

$C_{21}H_{15}O_3N$  requires  $N = 4.25$  per cent.

The alkaline filtrate from the tribenzamide was carefully treated with hydrochloric acid until the pyridine was nearly neutralised. A mass of white, silky needles came down, which were filtered and washed successively with sodium hydrogen carbonate solution and water. The needles, which melted at 143–146°, and, after recrystallisation from alcohol, at 148°, consisted of pure dibenzamide, the yield being 6 grams.

The aqueous filtrate from the dibenzamide in the above treatment yielded 12.5 grams of benzoic acid on acidification; no appreciable quantity of benzamide was recovered.

(2) *In presence of Benzene*.—Varying proportions of sodium benzamide and benzoic anhydride were taken in different experiments. The former, suspended in 10 times its weight of benzene, was quickly treated with a benzene solution of the anhydride and the mixture rapidly shaken. The resulting milky liquid became hot and almost immediately set to a stiff, white paste consisting chiefly of sodium-dibenzamide and benzoate, together with free benzamide and tribenzamide. The yield of dibenzamide isolated from the sodium derivative varied between 60 and 70 per cent. of the theoretical amount when 2 mols. of sodium benzamide to 1 mol. of benzoic anhydride were taken. The quantity of tribenzamide, which was isolated as a white, amorphous powder (m. p. 202°), was much smaller than that found in the pyridine experiments, whilst the amount of benzamide recovered was much larger.

*Benzoic Anhydride and Sodium Dibenzamide*.—A reaction set in on adding 5.5 grams of dibenzamide to 0.8 gram of finely powdered sodamide suspended in 40 grams of benzene; the mixture became hot, ammonia was evolved, and a white jelly of sodium dibenzamide was formed. The reflux apparatus was then heated at 90° for half an hour, during which time the sodium derivative became granular and crystalline; 5.5 grams of benzoic anhydride (1 mol. : 1 mol. sodium dibenzamide) dissolved in 10 grams of benzene were now added; no appreciable action occurred in the cold, but slow condensation took place on warming, and the contents of the flask were heated for 3 hours in a water-bath. After distilling off the benzene, a white solid remained, which was treated with water and filtered from a mass of insoluble needles. The filtrate contained practically nothing but sodium benzoate. The needles, which were contaminated with some adherent benzoic anhydride, consisted of both dibenzamide and tribenzamide, which were separated by treatment with aqueous sodium hydroxide and filtering. From the filtrate, 2 grams of dibenzamide

(m. p. 144—148°) were recovered. The white microcrystalline residue, insoluble in sodium hydroxide solution, was washed with alcohol and boiling water; it melted at 204—205° and consisted of pure tribenzamide (weight 2·5 grams).

0·2099 gave 7·9 c.c. moist nitrogen at 23° and 766 mm.  $N = 4·27$ .

\* By Kjeldahl's method: 0·2680 required 8·5 c.c.  $N/10$  HCl.  $N = 4·40$ .

$C_{21}H_{15}O_3N$  requires  $N = 4·25$  per cent.

*Succinic Anhydride and Sodium Benzamide. Benzoylsuccinamic Acid,*  
 $NHBz \cdot CO \cdot CH_2 \cdot CH_2 \cdot CO_2H$ .

Twelve grams of benzamide and 4 grams of sodamide were converted into sodium benzamide (1 mol.) and suspended in 150 c.c. of benzene, 10 grams of finely powdered succinic anhydride (1 mol.) added, and the mixture well shaken. Owing to the sparing solubility of the anhydride in benzene, the condensation proceeds only very slowly and with little heat development, unless the mixture is warmed. If heated quickly, it was found that the reaction was too energetic, and the best results were obtained by immersing the flask, attached to a reflux condenser, in a bath at 50° for 1½ hours. A steady, continuous change took place, the mixture became discoloured, and the reaction was finally completed by heating for 2 hours at 80—90°, at the end of which time a dirty-looking gelatinous mass was formed. The benzene was removed as completely as possible on the water-bath, and the residual solid, after cooling, was treated with about 100 c.c. of cold water. The insoluble part was removed by filtration. The soluble portion contained succinic and benzoic acids both free and as sodium salts and some benzamide. The insoluble residue contained a large quantity of benzamide together with two other substances. One of these was extracted by digesting with aqueous sodium carbonate, and the other by treating the remaining insoluble portion with sodium hydroxide. The final residue after this treatment was carefully examined and was shown to be practically pure benzamide, melting after recrystallisation from hot water at 129°.

The sodium carbonate extract and washings contained an acid which, by adding hydrochloric acid, was obtained as a dirty-white precipitate; this crystallised from boiling alcohol in needles, which

\* Two determinations of nitrogen by this method gave no result whatever, because tribenzamide resists the action of boiling sulphuric acid in presence of potassium sulphate even at the highest temperatures. With the aid of potassium permanganate, however, the decomposition was rendered complete and the above result thus obtained.

were still discoloured and melted at  $179^{\circ}$ . The acid was finally purified by crystallising from water containing animal charcoal, and obtained as clusters of large, colourless prisms melting at  $180^{\circ}$ . The yield was 3.25 grams and the compound was proved to be *benzoylsuccinamic acid*.

0.2176 gave 12.75 c.c. moist nitrogen at  $22^{\circ}$  and 749 mm.  $N = 6.54$ .

$C_{11}H_{11}O_4N$  requires  $N = 6.33$  per cent.

0.1694 required 8.15 c.c.  $N/10$  NaOH. M. W. = 210.

$C_{11}H_{11}O_4N$  requires M. W. = 221.

Benzoylsuccinamic acid is sparingly soluble in water and cold alcohol, and is decomposed by heating with sodium hydroxide forming benzamide, sodium succinate, and sodium benzoate. The *silver* salt comes down as a white, crystalline precipitate from neutral and not too dilute solutions on adding silver nitrate; it is sparingly soluble in cold water.

*s*-Dibenzoylsuccinamide,  $NHBz \cdot CO \cdot CH_2 \cdot CH_2 \cdot CO \cdot NHBz$ .

This compound is formed in small quantities in the interaction of succinic anhydride and sodium benzamide, and may be obtained by acidifying the caustic soda extract in the foregoing treatment. A better yield is obtained when 2 mols. of sodium benzamide to 1 mol. of succinic anhydride are taken; the two were brought into interaction in presence of benzene as before, and finally, while hot, the dark, granular solid was removed by filtration from the benzene, which, on cooling, deposited benzamide. The solid was dried on absorbent material and allowed to take up carbon dioxide from the air; it was then treated with water. The sodium salt of benzoylsuccinamic acid and other soluble products were removed by filtration from the greyish-white insoluble solid. The latter consisted chiefly of dibenzoylsuccinamide, which was freed from benzamide by digesting with boiling water and subsequent washing with cold alcohol; it remained behind as a nearly white powder, and was finally purified by dissolving in sodium hydroxide solution and filtering into dilute hydrochloric acid, when it was precipitated as an amorphous, white powder. The yield was small, being barely 10 per cent., inasmuch as the chief reaction led to the formation of benzoylsuccinamic acid.

0.0632 gave 4.85 c.c. moist nitrogen at  $22^{\circ}$  and 953 mm.  $N = 8.61$ .

$C_{18}H_{16}O_4N_2$  requires  $N = 8.64$  per cent.

Dibenzoylsuccinamide melts and darkens at  $211^{\circ}$ , is slowly but completely soluble in aqueous sodium hydroxide, forming the disodium

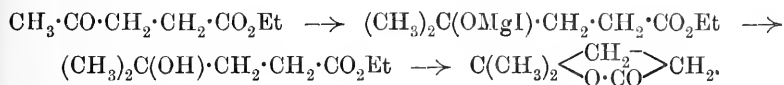
derivative; it is insoluble in hot water, benzene, chloroform, and ordinary organic solvents, but dissolves sparingly in boiling alcohol, from which it separates on cooling as a microcrystalline powder.

THE UNIVERSITY,  
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# CLXX.—A New Synthesis of isoCaprolactone and Certain Derivatives.

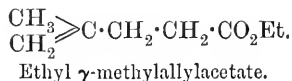
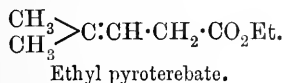
By DAVID TREVOR JONES and GEORGE TATTERSALL.

In a recent paper (*Compt. rend.*, 1902, 135, 629), Grignard described the application of his magnesium reaction to the formation of the lactone of  $\gamma$ -hydroxy- $\gamma$ -ethylvaleric acid from ethyl lævulate and magnesium ethyl iodide. Wishing to prepare a quantity of the corresponding methyl compound, isocaprolactone, for some synthetical experiments, the authors found that this lactone might be readily obtained in a yield of 30 per cent. by a similar process from ethyl lævulate and magnesium methyl iodide in accordance with the following scheme :



All attempts to prepare  $\gamma$ -bromoisocaproic acid from isocaprolactone by treatment with strong aqueous hydrobromic acid under varied conditions gave only negative results; treatment with alcoholic hydrobromic acid has, however been shown to yield ethyl  $\gamma$ -bromoisocaproate (Desfontaines, *Compt. rend.*, 1902, 134, 295).

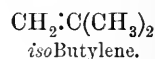
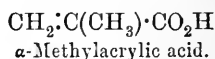
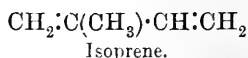
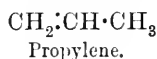
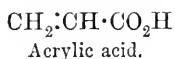
When treated successively with phosphorus pentabromide and alcohol, isocaprolactone is converted into ethyl  $\gamma$ -bromoisocaproate,  $\text{CMe}_2\text{Br} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$ , and this, on digesting with diethylaniline, is decomposed with the elimination of hydrogen bromide and the formation of an unsaturated ester, for the constitution of which there are two possibilities :



In the former case, boiling with concentrated caustic soda would not only hydrolyse the ester, but, at the same time, bring about a

transference of the double linking from the  $\beta\gamma$ - to the  $\alpha\beta$ -position (Fittig, *Annalen*, 1894, 283, 47, 269) so that  $\Delta^{\alpha}$ -isohexenoic acid,  $\text{Me}_2\text{CH}\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{H}$ , would be produced. In the latter case, simple hydrolysis would take place and  $\gamma$ -methylallylacetic acid, an acid which has not been previously described, would be obtained.  $\Delta^{\alpha}$ -isohexenoic acid has been obtained by Braun (*Monatsh.*, 1898, 17, 213) and by Franke and Kohn (*loc. cit.*, 1901, 20, 883), and these authorities agree in describing this acid as distilling without decomposition even under the ordinary pressure.

The acid obtained in the present investigation exhibited quite different properties, since it decomposed or polymerised considerably even on distillation under reduced pressure. There can, therefore, be little doubt that it is  $\gamma$ -methylallylacetic acid. The property of polymerising shown by the acid,  $\text{CH}_2:\text{CMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , is rather remarkable when it is remembered that its lower homologue, allylacetic acid,  $\text{CH}_2:\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , distils unchanged under the ordinary pressure. There exist, however, several cases analogous to this in which a compound containing the group  $\text{CH}_2:\text{CH}\cdot\text{C}$  is stable and does not polymerise under conditions which cause polymerisation of similar substances containing the group  $\text{CH}_2:\text{C} < \overset{\text{C}}{\text{O}}$ . The following short table illustrates this point; the compounds in the first column do not polymerise, whereas those in the second readily do so.



## EXPERIMENTAL.

### *Preparation of isoCaprolactone.*

In preparing the lactone, ethyl lævulate (36 grams) mixed with about four times its volume of dry ether was slowly added to a well-cooled ethereal solution of magnesium methyl iodide (prepared from 7 grams of magnesium and 40 grams of methyl iodide). After about an hour, the resulting magnesium compound was decomposed by cautiously adding water and dilute sulphuric acid. The ethereal layer was then separated and the acid solution extracted twice with small quantities of ether. The mixed ethereal extracts were washed with a little sodium hydrogen sulphite solution to remove iodine and afterwards dried over calcium chloride and evaporated. On distilling

the residual yellow oil under reduced pressure (100 mm.), most of it passed over between 85° and 140°, and on repeated fractionation a quantity of oil was obtained distilling at 140—150°/100 mm., which on examination was found to consist of a mixture of *isocapro*lactone with much unchanged ethyl *lævulate*.

In order to separate these substances, the oil was hydrolysed with alcoholic potash; water was then added and the solution evaporated until free from alcohol. The concentrated liquid was acidified with excess of hydrochloric acid and heated for 15 minutes on the water-bath in order to convert the  $\gamma$ -hydroxy*isocaproic* acid into the lactone. After extracting several times with ether, the ethereal extract was washed with sodium carbonate to remove the *lævulic* acid, dried over calcium chloride and evaporated. The resulting crude oil yielded on distillation pure *isocapro*lactone boiling at 205—207°.

0.1674 gave 0.3864 CO<sub>2</sub> and 0.1323 H<sub>2</sub>O. C = 62.9; H = 8.7.

0.1860 „ 0.4285 CO<sub>2</sub> „ 0.1492 H<sub>2</sub>O. C = 62.8; H = 8.9.

C<sub>6</sub>H<sub>10</sub>O<sub>2</sub> requires C = 63.1; H = 8.7 per cent.

*Ethyl  $\gamma$ -Bromoisocaproate*, (CH<sub>3</sub>)<sub>2</sub>CB<sub>r</sub>·CH<sub>2</sub>·CH<sub>2</sub>·CO<sub>2</sub>Et.—*iso*Caprolactone (4 grams) was treated with phosphorus pentabromide (18 grams) at the ordinary temperature and the mixture left for 24 hours, when most of the pentabromide had disappeared. The mixture was then poured in a thin stream into excess of absolute alcohol, the flask being carefully cooled during the operation. After 12 hours, the product was mixed with water and extracted three times with ether; the ethereal extract was then washed with water and dilute sodium carbonate solution, dried over calcium chloride, evaporated, and the yellow residue was freed from ether by being kept for several days over sulphuric acid in a vacuum desiccator.

As the bromo-ester decomposed considerably even when distilled under greatly reduced pressure, an analysis of the undistilled oil was made, the result of which shows that the oil consists essentially of ethyl  $\gamma$ -bromoisocaproate.

0.1998 gave 0.1541 AgBr. Br = 32.8.

C<sub>7</sub>H<sub>13</sub>O<sub>2</sub>Br requires Br = 35.9 per cent.

*Ethyl  $\gamma$ -Methylallylacetate*, CH<sub>2</sub>:C(CH<sub>3</sub>)·CH<sub>2</sub>·CH<sub>2</sub>·CO<sub>2</sub>Et.—The foregoing bromo-ester was now mixed with twice its volume of freshly distilled diethylaniline and the mixture, after being heated at 150—160° for 10 minutes, cooled and poured into dilute hydrochloric acid; the acid solution was extracted with ether and the extract washed successively with hydrochloric acid and aqueous sodium carbonate, dried over calcium chloride and evaporated. The residual oil distilled at 98—100° under 57 mm. and at 85° under 20 mm. pressure.

0.1210 gave 0.2905  $\text{CO}_2$  and 0.1050  $\text{H}_2\text{O}$ .  $\text{C} = 65.5$ ;  $\text{H} = 9.6$ .

0.1485 „ 0.3597  $\text{CO}_2$  „ 0.1307  $\text{H}_2\text{O}$ .  $\text{C} = 66.1$ ;  $\text{H} = 9.8$ .

$\text{C}_8\text{H}_{14}\text{O}_2$  requires  $\text{C} = 67.5$ ;  $\text{H} = 9.8$  per cent.

The low value obtained for the carbon was found to be due to the presence of a trace of bromine which could not be entirely removed by treatment with diethylaniline.

Ethyl  $\gamma$ -methylallylacetate is a mobile, fragrant liquid, which in chloroform solution readily decolorises bromine.

*$\gamma$ -Methylallylacetic Acid*,  $\text{CH}_2\text{:C}(\text{CH}_3)\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ .—In order to obtain this acid, the ester just described was hydrolysed by boiling with 10 per cent. aqueous caustic soda (1 mol. ester to 10 mols.  $\text{NaOH}$ ) for 12 hours, in accordance with the instructions given by Fittig for the conversion of a  $\beta\gamma$ -unsaturated acid into the  $\alpha\beta$ -isomeride (*Annalen*, 1894, 283, 51, 269). The product was acidified with dilute sulphuric acid and extracted with ether, and, after evaporating, the pungent oil was distilled in steam; the distillate was extracted with ether, the ethereal solution dried over calcium chloride, and evaporated. As the residue was found to decompose on distilling even under reduced pressure—a resinous substance remaining in the flask—no direct analysis of the acid was made, and a second experiment was carried out as follows:—The acid extracted with ether from the steam distillate was dissolved in ammonia and the silver salt obtained by precipitating with silver nitrate. The white, curdy precipitate was washed and dried under reduced pressure over sulphuric acid, the desiccator being kept in the dark because the salt is rapidly discoloured by light.

0.1897 gave 0.0930  $\text{Ag}$ .  $\text{Ag} = 48.9$ .

$\text{C}_6\text{H}_9\text{O}_2\text{Ag}$  requires  $\text{Ag} = 48.8$  per cent.

We hope to prepare large quantities of this and some other similarly constituted acids and subject them to a more detailed examination.

In conclusion, the authors desire to express their thanks to the Research Fund Committee of the Chemical Society for a grant with the aid of which these experiments were carried out.

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CLXXI.—*Amidechloroiodides.*

By GEORGE DRUCE LANDER and HARRY EDWIN LAWS

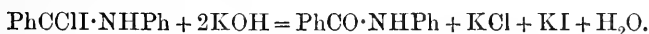
It seemed possible that when pure dry hydrogen iodide acts on the imidechloride of benzanilide, replacement of the chlorine atom by iodine might occur, and that the resulting imide-iodide would then lose iodine and yield the dianil of benzil, thus:  $\text{PhCCl:NPh} + \text{HI} = \text{PhCI:NPh} + \text{HCl}$  and  $2\text{PhCI:NPh} = (\text{PhC:NPh})_2 + \text{I}_2$ .

We find, however, that hydrogen iodide yields an additive compound with the imidechloride, to which we are inclined, although direct experimental evidence is wanting, to ascribe the constitution of a mixed amide halide, in this case the chloroiodide corresponding with benzanilide,  $\text{PhCCl:NPh} + \text{HI} = \text{PhCClI:NHPh}$ .

*Action of Hydrogen Iodide on Benzophenylimidechloride.*

A current of pure dry hydrogen iodide, purified by means of moist amorphous phosphorus and phosphoric oxide, was passed into a solution of benzophenylimidechloride at the ordinary temperature. A lemon-yellow, microcrystalline precipitate of the amidechloroiodide was at once produced, and was filtered, washed with light petroleum, and dried in a vacuum. The substance is moderately stable, but slowly acquires a green colour on keeping, and is only sparingly soluble in organic solvents, from which it cannot be recrystallised without undergoing alteration. The maximum degree of purity can therefore only be secured by employing the imidechloride in as pure a condition as possible, the absence of phosphorus chlorides being especially necessary. The compound decomposes energetically at  $106^\circ$ , when hydrogen chloride and iodide are given off, leaving a dark brown residue, the composition of which has not been determined.

When warmed with alcoholic potash, benzanilide and a mixture of potassium halides are formed:



The halogens were estimated in a weighed quantity in this way.

0.2440 required 0.15012 Ag and gave 0.2650 AgCl + AgI. Cl = 9.7; I = 37.3.

0.3852 gave 12.8 c.c. moist nitrogen at  $14^\circ$  and 772 mm. N = 4.0.

$\text{C}_6\text{H}_5\cdot\text{CClI}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$  requires Cl = 10.35; I = 37.0; N = 4.1 per cent.

Considering the difficulty of purification, we think that the experi-

mental figures agree sufficiently with those calculated to establish the composition.

*Benzo-p-tolylamidechloriodide*,  $C_6H_5 \cdot CClI \cdot NH \cdot C_7H_7$ , was prepared in a similar manner; it decomposes at  $130^\circ$  and resembles the phenyl analogue in all respects. On analysis, it gave  $N = 6.6$  instead of the calculated  $N = 6.7$  per cent.

### *Reactions of the Amidechloriodides.*

With water and, as already stated, with potassium hydroxide the amidechloriodides yield the parent amide and halogen hydrides or their salts.

When benzophenylamidechloriodide is dropped into an alcoholic solution of pure sodium ethoxide, *N*-phenylbenziminioethyl ether is formed,  $PhCClI \cdot NHPh + 2NaOEt = PhC(OEt) : NPh + NaCl + NaI + HOEt$ , as was shown by adding water and extracting with ether, when the ethereal extract, on evaporation, left an oil which, on boiling with dilute hydrochloric acid, gave aniline and ethyl benzoate, the characteristic products of the hydrolysis of the imino-ether. A little benz-anilide also resulted from the action of the ethoxide.

With aniline (3 mols.) in benzene solution, diphenylbenzenylamidine and aniline hydrohalides are formed. The amidine melted after crystallisation from alcohol at  $129^\circ$ , and gave  $N = 10.4$  instead of the calculated  $N = 10.3$  per cent.

It will be observed that in no case could evidence of the position of the iodine atom in the molecule be obtained from reactions of replacement. Supposing, however, that in the reactions with sodium ethoxide and aniline the compounds  $PhC(OEt)_2 \cdot NHPh$  and  $PhC(NHPh)_3$  had been formed, there can be no doubt (compare this vol., p. 986) that they would most readily part with alcohol and aniline, yielding the imino-ether and amidine respectively. At the same time, it must be remarked that the amidechloriodide differs in physical properties, and particularly in respect to its stability on warming, from its congener benzophenylamidechloride,  $PhCCl_2 \cdot NHPh$ , a substance which parts so readily with hydrogen chloride, forming the imidechloride, that it is prepared only with great difficulty, and, so far as we know, it is not formed when hydrogen chloride acts on the imidechloride.

Our amidechloriodides are also analogous to the imidedi-iodides prepared by Biltz from the nitriles by means of concentrated hydriodic acid solution (*Ber.*, 1892, 25, 2533). In these compounds, the hydrogen iodide is most readily dissociated from the molecule, yielding the nitriles, although benzamidedi-iodide with phenol gives benzaurine, a reaction which favours the given formula, but which could be explained in other ways, as, for example, a condensation dependent on the elimin-

ation of ammonia between benzonitrile and phenol in the presence of acid.

The amideiodides of Biltz can be easily prepared by our method. We find also that, with sodium ethoxide, benzamidedi-iodide gives benzonitrile, a reaction not examined by Biltz.

The only alternative structure for the amidechloroiodide would be that of a salt of the type  $\text{PhCCl:NHPhI}$ , for which, however, there is no analogy, especially when the anil group is attached to so negative a residue as  $\text{PhCCl}$ .

We are at present engaged in attempts to prepare other ortho-compounds of a similar kind to those described in this note.

Much of the expense of this work was defrayed by a grant made from the Research Fund, for which we desire to express our indebtedness.

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CLXXII.—*The Decomposition of Ethylene Iodide under the Influence of the Iodide Ion.*

By ARTHUR SLATOR, Ph.D.

WHEN crystals of iodine are exposed to an atmosphere of ethylene, ethylene iodide is slowly formed, whilst when the pure iodide is kept for some time it turns brown and crystals of iodine make their appearance. This formation and decomposition of ethylene iodide at the same temperature shows that in the gaseous phase the equilibrium point of the change represented by  $\text{C}_2\text{H}_4\text{I}_2 \rightleftharpoons \text{C}_2\text{H}_4 + \text{I}_2$  is appreciably removed from both ends of the reaction. In solutions of these substances another such equilibrium is probably established. If one of the products of reaction is removed from the system, it is clear that a complete decomposition could be observed. In the present communication, the catalytic decomposition of the iodide is investigated under conditions such that the reaction is practically completed.

In the study of the reactions between this iodide and sodium thiosulphate described in a previous paper (this vol., p. 1286), it was observed that when the experiments were carried out with excess of the iodide the solutions, after all the thiosulphate had reacted, soon became brown. This liberation of iodine from the excess of

iodide was found to be due to the sodium iodide formed in the primary reaction, and further investigation showed that solutions of ethylene iodide easily decompose in the presence of certain metallic iodides. Qualitative experiments indicated that the decomposition is accelerated, not only by iodides, but also, although to a much less extent, by bromides, whilst the influence of chlorides is very slight. Nitric acid and the following salts: copper sulphate, potassium chlorate, stannous chloride, and ferrous sulphate have practically no effect on this decomposition. Bright sunlight increases the velocity of the reaction.

The influence of the iodides was so marked that quantitative experiments were made to investigate the amount of iodine liberated in the reaction. An alcoholic solution of ethylene iodide of known strength was decomposed by the addition of a strong solution of potassium iodide, and after the completion of the reaction the amount of free iodine was titrated by standard thiosulphate solution. The following table shows that practically the whole of the iodine is liberated from small quantities of ethylene iodide if the concentration of potassium iodide is greater than N/15.

TABLE I.

$C_2H_4I_2$ .	I liberated in c.c. N/100 solution.		Ratio. $C_2H_4I_2 : I_2$ .
	Found.	Calculated.	
Gram.	c.c.	c.c.	
0.0329	22.6	23.3	1 : 0.97
0.0500	34.9	35.5	1 : 0.98
0.0464	32.4	33.0	1 : 0.98
0.0343	23.9	24.3	1 : 0.98
0.0455	32.9	32.3	1 : 1.01
0.0419	29.4	29.7	1 : 0.99
0.0419	29.7	29.7	1 : 1.00
0.0440	31.4	31.2	1 : 1.01
Mean .....			1 : 0.99

With smaller concentrations of potassium iodide, the total amount of iodine is not liberated; this difference is probably due either to the potassium iodide forming tri-iodide and being removed from the system or to some secondary reaction. Other experiments were carried out to show qualitatively that ethylene is liberated in the reaction. A test-tube containing a mixture of potassium iodide and ethylene iodide was immersed in mercury to displace the air and then inverted over the liquid. About 2 c.c. of a mixture of alcohol and water were introduced into the tube, and after shaking some time a gas collected over the solution which was proved to be ethylene by its action on bromine water.

We may therefore conclude that the reaction under consideration is

the decomposition of ethylene iodide according to the equation  $C_2H_4I_2 = C_2H_4 + I_2$ . The action of the metallic iodide still remained to be investigated. From these preliminary experiments it is uncertain whether the iodide merely removes the free iodine as it is formed and hence helps the decomposition, or whether the influence is of a more profound character. Measurement of the velocity of the reaction seemed to be the simplest method of testing these possibilities, and the chief part of this paper is devoted to a description of such measurements. Titration of the free iodine, which is formed in the reaction, affords a ready means of following the change. The experiments are carried out in flasks placed in a thermostat, which is regulated at a suitable temperature. The solvent used in all these experiments is a mixture of alcohol and water (5 c.c. alcohol to 2 c.c. water). An alcoholic solution of ethylene iodide is prepared, the requisite quantity of water added, and after allowing the solution to acquire the temperature of the thermostat a weighed quantity of potassium iodide is introduced and the flask rapidly shaken so as to dissolve the solid. At suitable intervals of time, 5 c.c. of the mixture are taken out by means of a pipette and titrated with  $N/100$  sodium thiosulphate.

Measurements obtained by such means show that the velocity of decomposition is proportional to the concentration of the ethylene iodide and approximately proportional to that of the potassium iodide. Free iodine in the solution has the effect of retarding the reaction, and therefore, in calculating the constants of the reaction, only initial velocities have been considered. When strong ( $N/10$ ) solutions of potassium iodide are used, the formation of free iodine causes no appreciable disturbance in the first third of the reaction. The final titre of iodine also agrees with that calculated from the initial concentration of ethylene iodide. With more dilute ( $N/40$ ) solutions of potassium iodide, the influence of the iodine is very soon noticeable; the calculated end point of the reaction is in these cases used to obtain the values of the velocity constants.

In the following tables:— $t$  = time in minutes, (I) = iodine titre obtained by titrating 5 c.c. of solution with approximately  $N/100$  thiosulphate solution,  $(C_2H_4I_2)$  = ethylene iodide titre = difference of final iodine titre and that after time  $t$ .

The constants  $K$  are obtained from the last column of figures by the formula for a unimolecular reaction  $K = \frac{1}{t} \log C_0/C_t$  where  $C_0$  = initial value of  $(C_2H_4I_2)$  and  $C_t$  = value of time  $t$ .

In Table II,  $n$  is the order of the reaction in relation to the ethylene iodide, and is calculated by the usual formula:

$$n = \frac{\log dc_1/dt - \log dc_2/dt}{\log C_1 - \log C_2},$$

where  $dc_1/dt$ ,  $dc_2/dt$  are the velocities at concentrations  $C_1$  and  $C_2$ .

These tables show that, within the experimental limits,  $n$  is equal to 1 and is independent of the concentration of potassium iodide. The values of  $K$  are approximately proportional to the concentration of this iodide and increase to about 2.5 times their former value for a temperature rise of  $10^\circ$ .

TABLE II.

*Influence of  $C_2H_4I_2$ -concentration.*

Temperature =  $25^\circ$ .

KI-concentration = 0.100 N.

$t$ .	(I).	$(C_2H_4I_2)$ .	$K$ .	$t$ .	(I).	$(C_2H_4I_2)$ .	$K$ .
0	1.3*	34.1	—	0	0.55*	17.15	—
10	5.1*	30.3	0.0051	15	3.4*	14.3	0.0053
20	8.4	27.0	0.0051	30	5.75	11.95	0.0052
30	11.25	24.15	0.0050	50	8.2	9.5	0.0051
$\infty$	35.4	0	—	$\infty$	17.7	0	—

$n$  (calculated from titrations\*) = 0.95.

From other experiments:

KI-concentration 0.0961 N,  $n = 1.05$   
 ,, 0.0462 N,  $n = 1.00$

KI-concentration 0.0276 N,  $n = 1.10$   
 ,, 0.0250 N,  $n = 1.05$

TABLE III.

*Influence of KI-concentration.*

Temperature =  $25^\circ$ .

KI-concentration = 0.1302 N.

$t$ .	(I).	$(C_2H_4I_2)$ .	$K$ .
0	0.8	30.3	—
10	4.7	26.4	0.0060
20	8.3	22.8	0.0062
30	11.3	19.8	0.0062
$\infty$	31.1	0	—

KI-concentration = 0.0540 N.

$t$ .	(I).	$(C_2H_4I_2)$ .	$K$ .
0	0.9	30.2	—
10	2.8	28.3	0.0028
25	5.7	25.4	0.0030
45	8.6	22.5	0.0028
$\infty$	31.1	0	—

KI-concentration = 0.0718 N.

$t$ .	(I).	$(C_2H_4I_2)$ .	$K$ .
0	0.5	32.7	—
10	3.4	29.8	0.0040
20	5.7	27.5	0.0038
35	9.15	24.05	0.0038
$\infty$	33.2	0	—

KI-concentration = 0.0250 N.

$t$ .	(I).	$(C_2H_4I_2)$ .	$K$ .
0	0.4	35.0	—
20	2.7	32.7	0.00148
50	5.55	29.85	0.00138
120	10.3	25.1	0.00120
$\infty$	35.4	0	—

TABLE III (*continued*).

KI-concentration.	$K$ .	1000K/KI-concentration.
0.1302 <i>N</i>	0.0061	47
0.1043	0.0052	50
0.1000	0.0051	51
0.0961	0.0049	51
0.0718	0.0039	54
0.0540	0.0029	54
0.0276	0.00167	61
0.0250	0.00148	59

TABLE IV.

*Influence of Temperature.*

Temperature = 35°.

KI-concentration = 0.100 <i>N</i> .				KI-concentration = 0.075 <i>N</i> .			
$t$ .	(I).	(C <sub>2</sub> H <sub>4</sub> I <sub>2</sub> ).	$K$ .	$t$ .	(I).	(C <sub>2</sub> H <sub>4</sub> I <sub>2</sub> ).	$K$ .
0	1.3	27.0	—	0	2.9	30.9	—
5	5.05	23.25	0.0130	5	6.4	27.4	0.0104
15	10.9	17.4	0.0127	15	11.85	21.95	0.0099
25	15.2	13.1	0.0126	25	15.9	17.9	0.0095
∞	28.3	0	—	∞	33.8	0	—
$K_{35} = 0.0127$ .				$K_{35} = 0.0104$ .			
$K_{25} = 0.0051$ .				$K_{25} = 0.0041$ .			

Temperature quotient = 2.5.

Temperature quotient = 2.55.

We may conclude from these measurements that the accelerative influence of potassium iodide is not merely due to the removal of free iodine from the solution, for if such were the case the initial velocities would (within certain limits) be independent of the concentration of this salt. The velocity constants are approximately proportional to the concentration of the potassium iodide, showing that the salt takes either a direct or a catalytic part in the reaction.

The value  $\frac{K}{\text{KI-concentration}}$  (Table III) shows a slight increase with increasing dilution, suggesting that the I<sup>-</sup> ion is the important factor in determining the velocity of reaction. This observation is confirmed by other measurements; it is found that sodium and ammonium iodides, which are dissociated to about the same extent as potassium iodide, have approximately the same accelerative influence in equivalent solutions, whereas salts such as cadmium iodide, which are known to be less dissociated, are much less active, and the addition of such substances as iodine and mercury iodide, which form complexes with the I<sup>-</sup> ion, greatly decreases the activity of potassium iodide.

TABLE V.—Temperature = 25°.

NaI-concentration = 0.100 <i>N</i> .				NH <sub>4</sub> I-concentration = 0.100 <i>N</i> .			
<i>t</i> .	(I).	(C <sub>2</sub> H <sub>4</sub> I <sub>2</sub> ).	<i>K</i> .	<i>t</i> .	(I).	(C <sub>2</sub> H <sub>4</sub> I <sub>2</sub> ).	<i>K</i> .
0	0.75	28.55	—	0	1.7	29.4	—
10	3.95	25.35	0.00515	10	4.9	26.2	0.0050
20	6.7	22.6	0.0051	20	7.8	23.3	0.0050
30	9.1	20.2	0.0050	35	11.2	19.9	0.0048
∞	29.3	0	—	∞	31.1	0	—

KI-concentration = 0.100 *N*. . . . . *K* = 0.0051 (Table II).

TABLE VI.

Catalyser.	$\Delta c/\Delta t$ .	Catalyser.	$\Delta c/\Delta t$ .
0.100 KI .....	0.32	0.072 KI + 0.071 I .....	0.14
0.100 NH <sub>4</sub> I .....	0.32	0.036 KI + 0.059 I .....	0.032
0.100 KI + 0.100 HCl .....	0.25	0.036 KI + 0.162 I .....	0.018
0.100 CdI <sub>2</sub> /2 .....	0.011	0.100 NaBr .....	0.006
0.100 K <sub>2</sub> HgI <sub>4</sub> /2 .....	0.012	Without catalyser .....	< 0.0001
0.072 KI .....	0.25		

The initial velocities of reaction ( $\Delta c/\Delta t$ , Table VI) show a great variation with different catalysers. Thus, cadmium iodide and mercuric potassium iodide have only about 1/30th of the activity of potassium or ammonium iodide. Hydrogen iodide has less influence than potassium iodide, for the addition of hydrochloric acid to potassium iodide lowers the velocity by about 20 per cent. Addition of iodine to potassium iodide in the proportion I : KI decreases the activity of the iodide by nearly one-half, a further addition has less effect, and a mixture in the proportion I<sub>2</sub> : KI still has an accelerative action. Bromides have about 1/50th of the activity of iodides.

The results obtained from the foregoing experiments may be summarised by the equation  $dI/dt = K \cdot C_{C_2H_4I_2} \cdot C_{I'}$ , that is, the rate of formation of free iodine is proportional to the concentration of the ethylene iodide and the I'-ion. More than one reaction can be constructed which agrees with this result; thus the change measured under these conditions may be a direct action of the I'-ion on the organic iodide according to the equation  $C_2H_4I_2 + I' = C_2H_4 + I'_3$ . The direct formation of the I'<sub>3</sub>-ion is, however, not very probable. The I'-ion may be considered to be a catalytic agent which accelerates the decomposition of the organic iodide, and, until further evidence is brought forward to explain the mechanism of the reaction, it is perhaps the most convenient view to adopt.

In a previous communication (this vol., pp. 1297) it has been shown that sodium thiosulphate has a direct action on ethylene iodide, and that the action is bimolecular. The change which is here measured is probably  $C_2H_4I_2 + Na_2S_2O_3 \rightarrow C_2H_4I \cdot NaS_2O_3 + NaI$ , and is followed

by a rapid reaction between the iodo-ester and another equivalent of sodium thiosulphate.\*

Experiments were carried out to investigate whether this reaction is in any way connected with the decomposition of ethylene iodide by the action of potassium iodide. If sodium thiosulphate, potassium iodide, and ethylene iodide are brought together in solution, we should expect the thiosulphate to be used up partly by acting directly on the organic iodide and partly by interaction with the liberated iodine. If the two reactions have no influence on each other, the rate of disappearance of thiosulphate would be determined by the sum of the velocities of the two single reactions. If, however, interference took place, this agreement would not be observed.

Experiments carried out to detect any such influence show that the observed rate and that calculated from the velocity of the single reactions agree approximately, and we may therefore assume that the reactions are distinct from one another and may be superimposed without appreciable interference.

A solution containing the three reagents was prepared, taking care to have excess of ethylene iodide. The time which elapsed from the mixing of the solutions to the appearance of free iodine was measured and compared with the value calculated from the known velocity of the single reactions.

Assuming no interference of the reactions, the rate at which thiosulphate disappears is given by the following equation :

$$-dx/dt = K_1 x(x+a) + K_2(x+a) \quad . \quad . \quad (1)$$

where

$x$  and  $x+a$  represent the concentrations of thiosulphate and ethylene iodide respectively, and  $K_1$  and  $K_2$  = velocity constants of the two single reactions.

Integration of equation (1) gives

$$0.4343 K_1(a - K_2/K_1)t = \log \frac{x+a}{x + K_2/K_1} + \text{constant}.$$

If  $x = x_0$  when  $t = 0$

$$\text{the constant} = -\log \frac{x_0+a}{x_0 + K_2/K_1}.$$

Substituting and calculating the time for  $x=0$ , we get

$$t = \frac{\log \frac{aK_1(x_0 + K_2/K_1)}{K_2(x_0+a)}}{0.4343 K_1(a - K_2/K_1)} \quad . \quad . \quad . \quad (2)$$

\* Some ethylene is liberated in this reaction and also in the reaction between ethylene bromiodide and sodium thiosulphate. The product in these two reactions is, therefore, not wholly sodium ethylene thiosulphate.

If, therefore, ethylene iodide is in excess, the time when free iodine will appear is given by formula (2), where  $x_0$  and  $x_0 + a$  represent the initial concentrations of thiosulphate and ethylene iodide respectively, and where  $a$  = excess of ethylene iodide, expressed in gram-equivalents per litre.

The measurements were carried out by mixing 5 c.c. of an alcoholic ethylene iodide solution with 2 c.c. of an aqueous solution of sodium thiosulphate and potassium iodide. The temperature of the two solutions was so arranged that, on mixing, the aqueous alcoholic solution was about  $25^\circ$ . The tube containing the mixture was vigorously shaken in the water of the thermostat to bring the contents exactly to  $25^\circ$ .

The solution was allowed to remain in the thermostat and watched until the faint yellow colour of free iodine made its appearance. It may be noted that starch is useless as an indicator in these aqueous alcoholic solutions. The yellow coloration is, however, distinct enough to give consistent results, as is shown by the following table :

TABLE VII.

Temperature =  $25^\circ$ . KI-concentration = 0.100 *N*.

$$0.4343 K_1 = 0.99 \quad (\text{Table XII, p. 1293}).$$

$$0.4343 K_2 = 0.0051 \quad ( \quad , \quad \text{II, p. 1700}).$$

$x_0$ .	$x_0 + a$ .	$a$ .	<i>t</i> .	
			Calculated.*	Observed.
0.0103	0.0419	0.0316	13.7 mins.	15.7, 15.7, 15.5 mins.
0.0106	0.0210	0.0104	34.5 "	40.9, 40.6 "
0.0105	0.0251	0.0146	26.4 "	31.3, 31.3, 31.1 "

KI-concentration = 0.050 *N*.

$$0.4343 K_1 = 0.99.$$

$$0.4343 K_2 = 0.00270.$$

$x_0$ .	$x_0 + a$ .	$a$ .	<i>t</i> .	
			Calculated.*	Observed.
0.0100	0.0484	0.0384	16.1 mins.	17.2, 17.3 mins.
0.0100	0.0242	0.0142	38.6 "	40.7, 40.8 "

The above table shows that with a *N*/10 solution of potassium iodide the calculated values of the time are about 16 per cent. lower than the observed values, whilst with a *N*/20 solution the difference is about 6 per cent. The approximate agreement shows that the reactions have

\* In this calculation the accelerating influence of the sodium iodide which is formed in the reaction has not been considered. This correction would make the calculated values about 3 per cent. smaller.

no great influence on each other, and the difference may be explained if we assume that the ions ( $S_2O_3^{''}, I'$ ) interact and the ionic concentrations are decreased by the addition of other salts.\*

It is a well-known fact that solutions of alkyl iodides if kept some time become brown owing to the liberation of iodine. The rate of the reaction depends on the constitution of the compound and is specially marked among the lower members of the series (K. A. Burke and F. G. Donnan, this vol., p. 574). Experiments were made to test whether these reactions were accelerated by potassium iodide. Test-tubes containing aqueous alcoholic solutions of the organic iodides and potassium iodide were kept and the coloration compared with that observed when no potassium iodide is added. The results obtained from experiments with methyl iodide, *isopropyl* iodide, and ethyl iodoacetate show a very appreciable acceleration, due to the presence of potassium iodide. These reactions are probably oxidations, for on excluding air from the mixture only faint yellow colorations could be obtained. It is possible that these reactions are in some way analogous to that of the decomposition of ethylene iodide, for both are accelerated by the addition of potassium iodide.

Iodine compounds in which two iodine atoms are united to adjacent carbon atoms show a special tendency to decompose, forming the olefinic compound and liberating free iodine. This is noticeable, not only in the case of ethylene iodide, but is evident in certain other reactions. Organic iodides are often prepared by the action of metallic iodides on the corresponding organic bromide or chloride. In these preparations, some free iodine is invariably liberated, especially in the presence of moisture. With the dihalogen compounds, this secondary reaction takes place to such an extent that the product is often entirely an ethylene compound and free iodine, thus  $\alpha\beta$ -dibromopropionic acid on treatment with potassium iodide gives acrylic acid, and not the di-iodide. These reactions are evidently closely related to the decomposition of organic iodides under the influence of metallic iodides, and the question arises whether, in these preparations, the di-iodide is first formed and then decomposed by a further action of potassium iodide, or whether the decomposition takes place without the intermediate formation of the di-iodide.

Ethylene bromiodide decomposes in presence of potassium iodide according to the equation  $C_2H_4BrI + KI = C_2H_4 + KBr + I_2$ , and this reaction was investigated with the view of determining whether ethylene iodide is an intermediate product or not. Measurements of the velocity of the reaction were carried out in a similar manner to

\* The velocity of reaction between methyl iodide and sodium thiosulphate is lowered about 10 per cent. by the addition of potassium iodide to form a *N*/10 solution (this vol., p. 1293).

that described in the case of ethylene iodide, and, as the following tables show, analogous results were obtained. The velocity is proportional to the bromiodide concentration and approximately to that of the potassium iodide. The temperature quotient is 2.45 for a rise of 10°. The rate of decomposition is about one-third of that of the ethylene iodide.

TABLE VIII.

Grams $C_2H_4BrI$ .	I liberated in c.c. $N/100$ solution.		Ratio. $C_2H_4BrI : I_2$ .
	Found.	Calculated.	
0.0251	21.0	21.4	1 : 0.98
0.0651	55.7	55.4	1 : 1.01

TABLE IX.

*The Influence of the Bromiodide Concentration.*

Temperature = 25°. KI-concentration = 0.1000  $N$ .

$t$ .	(I).	$(C_2H_4BrI)$ .	$K$ .	$t$ .	(I).	$(C_2H_4BrI)$ .	$K$ .
0	0.4*	20.3	—	0	0.2*	54.7	—
20	1.9	18.8	0.00167	15	3.2*	51.7	0.00163
49	3.8*	16.9	0.00162	40	7.3	47.6	0.00153
110	6.95	13.75	0.00154	60	10.1	44.8	0.00145
$\infty$	20.7	0	—	$\infty$	54.9	0	—

$n$  (calculated from titrations\*) = 1.00.

TABLE X.

*The Influence of Potassium Iodide Concentration.*

Temperature = 35°.

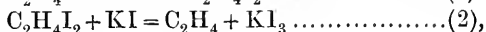
KI-concentration = 0.050 $N$ .				KI-concentration = 0.100 $N$ .			
$t$ .	(I).	$(C_2H_4BrI)$ .	$K$ .	$t$ .	(I).	$(C_2H_4BrI)$ .	$K$ .
0	0.15	20.55	—	0	0.4	20.3	—
30	3.0	17.7	0.00216	10	2.2	18.5	0.0041
60	5.0	15.7	0.00195	27	4.95	15.75	0.0041
125	8.65	12.05	0.00186	50	7.75	12.95	0.0039
$\infty$	20.7	0	—	$\infty$	20.7	0	—

KI-concentration = 0.150 $N$ .				1000 $K$ /KI-concentration.	
$t$ .	(I).	$(C_2H_4BrI)$ .	$K$ .	KI-concentration.	$K$ .
0	0.4	20.3	—	0.050 $N$	0.00216
25	6.25	14.45	0.0059	0.100	0.0041
40	8.65	12.05	0.0057	0.150	0.0059
$\infty$	20.7	0	—	Temperature quotient = 2.45.	

These results may be used for determining whether ethylene iodide

is an intermediate product of the reaction or not. If we assume that the reaction goes through the steps,



we have the following possibilities.

Reaction (1) may proceed much faster than (2) and the velocity measured would then be that of reaction (2). This is not the case, for reaction (2) proceeds with about three times the velocity measured in these experiments. Neither can we assume that the velocity of reaction (1) is incomparably smaller than that of (2), for then the measured velocity would be that of reaction (1) and the ratio of the two velocities would be 1:3. The only other possibility is that the two velocities are comparable and that the reactions are superimposed. If this were the case, the initial velocity of liberation of iodine would be zero. The rate would increase to a maximum and then decrease. Increase in the concentration of potassium iodide would probably increase the velocity of both reactions, and the rate of liberation of iodine would be proportional to the concentration of potassium iodide raised to a higher power than one.

Experimental evidence gives no indication of these results, and we may therefore assume that ethylene iodide is probably not an intermediate compound in the reaction. This result shows that it is possible for potassium iodide to have a direct action on organic chlorides and bromides, liberating iodine without the intermediate formation of the organic iodide.

### *Summary of Results.*

1. Ethylene iodide in aqueous alcoholic solution decomposes quantitatively in the presence of potassium iodide, yielding ethylene and iodine.

2. The velocity of reaction is proportional to the concentration of ethylene iodide and that of the  $\text{I}^-$ -ion, showing that the potassium iodide takes some direct (or catalytic) part in the reaction. The temperature for  $10^\circ$  is 2.5.

3. This reaction is quite distinct from that between ethylene iodide and sodium thiosulphate, for on carrying out the two reactions in the same solution the rate of disappearance of the thiosulphate is approximately equal to that calculated from the velocity of the two single reactions.

4. The rate of liberation of iodine from solutions of methyl iodide, isopropyl iodide, and ethyl iodoacetate is accelerated by the addition of potassium iodide.

5. Ethylene bromiodide in presence of potassium iodide liberates iodine according to the equation:  $C_2H_4IBr + KI = C_2H_4 + I_2 + KBr$ .

6. The velocity of the preceding reaction is proportional to the concentration of the bromiodide and to that of the potassium iodide, and the temperature quotient for  $10^\circ$  is 2.45. Ethylene iodide is probably not an intermediate product in this reaction. The iodide decomposes about three times as fast as the bromiodide.

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### CLXXIII.— $\Delta^a$ -Oleic Acid.

By HENRY RONDEL LE SUEUR.

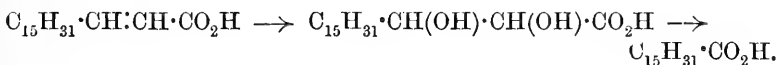
THE preparation of this acid, which has been mentioned in a former paper (this vol., p. 827), was undertaken in order to complete the study of a method for the determination of the constitution of fatty acids (compare Trans., 1899, 75, 161; 1900, 77, 83). The method consists in heating the  $\alpha$ -bromo-ester of the acid the constitution of which is to be determined with diethylaniline or quinoline, when an  $\alpha\beta$ -unsaturated ester is produced, which, on hydrolysis, yields the corresponding acid. This unsaturated acid is then successively oxidised with alkaline potassium permanganate and chromic acid, when an acid is obtained which contains two carbon atoms less than the original acid. In the case of those acids already investigated, it was customary to watch the progress of the elimination of the elements of hydrogen bromide by making use of the fact that the unsaturated acids readily absorbed bromine in the cold.

On submitting ethyl  $\alpha$ -bromostearate to the action of diethylaniline and quinoline, it was found that the product obtained, although free from bromine, did not absorb this element from its cold chloroform solution. It was then decided to try the action of alcoholic potash on  $\alpha$ -bromostearic acid in the hope that the  $\alpha\beta$ -unsaturated acid would be produced, and thus admit of an investigation of its properties.

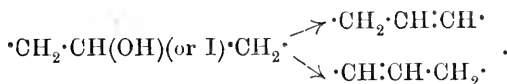
The action of alcoholic potash on  $\alpha$ -bromostearic acid has already been investigated by Hell and Sadomsky (*Ber.*, 1891, 24, 2391), who made use of this reaction for preparing  $\alpha$ -hydroxystearic acid. The

product isolated by these authors melted at  $84-85^\circ$ , and was undoubtedly contaminated with traces of the  $\alpha\beta$ -unsaturated acid, since, as the present author has already shown (*loc. cit.*), pure  $\alpha$ -hydroxystearic acid melts at  $91-92^\circ$ .

$\alpha$ -Bromostearic acid was heated with alcoholic potash in the manner described on p. 1711, and the resulting product submitted to a process of fractional crystallisation, when two acids were isolated, namely,  $\alpha$ -hydroxystearic acid melting at  $91-92^\circ$ , and a new acid,  $C_{18}H_{34}O_2$ , melting at  $58-59^\circ$ . That the latter acid has the molecular formula assigned to it is proved by analysis and determination of the molecular weight of its ethyl ester by the freezing point method. It is undoubtedly unsaturated, for although it does not absorb bromine in the cold, it readily reduces an alkaline solution of potassium permanganate with the production of a dihydroxystearic acid. The position of the double linking between the  $\alpha$ - and  $\beta$ -carbon atoms is proved by the fact that, on complete oxidation with potassium permanganate, it yields palmitic acid,



In 1888, M. C. Saytzeff and A. Saytzeff (*J. pr. Chem.*, 1888, [ii], 37, 269) prepared and described an acid melting at  $44-45^\circ$ , to which they assigned the above formula, and which they named *isoleic* acid. This substance they obtained from oleic acid by two different methods; the first consisted in the successive treatment of oleic acid with sulphuric acid and water, when a monohydroxystearic acid was obtained which, on distillation, gave two unsaturated acids—oleic and *isoleic* acids; the second method consisted in the addition of the elements of hydrogen iodide to oleic acid and treatment of the resulting iodostearic acid with alcoholic potash, when oleic and *isoleic* acids were again obtained. Since oleic and *isoleic* acids are formed from the same monohydroxystearic acid or iodostearic acid, the authors concluded that the double linking in both acids must be joined to a similarly situated carbon atom, and that the following grouping is common to both:



Now *isoleic* acid takes up the elements of hydrogen iodide, giving a liquid iodostearic acid which, on treatment with alcoholic potash, gives only one unsaturated acid, namely, *isoleic* acid, and from this the authors concluded that the iodine is attached to the  $\alpha$ -carbon atom,

and that the constitution of *isooleic* acid is represented by formula I and that of *oleic* acid by formula II:

$C_{14}H_{29} \cdot CH_2 \cdot CH_2 \cdot CHI \cdot CO_2H$ , iodostearic acid from *isooleic* acid.

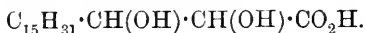
I.  $C_{14}H_{29} \cdot CH_2 \cdot CH : CH \cdot CO_2H$ , *isooleic* acid.

II.  $C_{14}H_{29} \cdot CH : CH \cdot CH_2 \cdot CO_2H$ , *oleic* acid.

The above iodostearic acid, when treated with silver oxide, gives a monohydroxy-derivative which melts at  $82-85^\circ$  and distils unchanged, a property which, the authors state, affords additional support to the statement that it is an  $\alpha$ -hydroxy-acid, and that the parent iodostearic acid is an  $\alpha$ -iodo-derivative. Now the present author has recently shown (this vol., p. 827) that  $\alpha$ -hydroxystearic acid melts at  $91-92^\circ$ , and, on distillation, yields margaric aldehyde; therefore the hydroxy-acid obtained by the Saytzeffs and the iodostearic acid from which it was prepared cannot be  $\alpha$ -derivatives.

Further, Ponzio (*Gazzetta*, 1904, 34, ii, 77) has recently prepared an iodostearic acid in which the iodine is undoubtedly in the  $\alpha$ -position, and this substance is a crystalline solid melting at  $66^\circ$ , and is therefore not identical with the so-called  $\alpha$ -iodostearic acid obtained by the Saytzeffs.

*isoOleic* acid readily absorbs bromine in the cold with the evolution of much heat and the formation of a liquid dibromo-acid, which, on treatment with silver oxide, gives a dihydroxy-acid melting at  $76-78^\circ$  and resolidifying at  $66-64^\circ$ , and which the authors state is more soluble in ether than the dihydroxystearic acid derived from *oleic* acid. This dihydroxy-acid was also obtained by the oxidation of *isooleic* acid with potassium permanganate. The  $\Delta^a$ -oleic acid described in the present communication does not absorb bromine in the cold, and on oxidation with potassium permanganate gives a dihydroxy-acid melting at  $126^\circ$  and resolidifying at  $124^\circ$ , and which dissolves only very slightly in ether, but is appreciably soluble in water, a property which is in agreement with its constitution, since it may be regarded as a substituted glyceric acid,



The fact that *isooleic* acid, on fusion with caustic potash, gives palmitic and acetic acids, affords no evidence as to its constitution, since *oleic* acid itself behaves in an exactly similar manner.

It is therefore evident that *isooleic* acid has not the double linking between the  $\alpha$ - and  $\beta$ -carbon atoms (formula I), and consequently the formula II assigned to *oleic* acid is in no way justified, since its validity entirely rests on the correctness of the formula given to *isooleic* acid.

This eliminates one of the two formulæ proposed for *oleic* acid,

and, from the work of Baruch (*Ber.*, 1894, 27, 172) and others, there is no doubt that the other formula, in which the double linking is situated between the 9th and 10th carbon atoms, correctly represents the constitution of this acid,  $\text{CH}_3(\text{CH}_2)_7\cdot\text{CH}:\text{CH}(\text{CH}_2)_7\cdot\text{CO}_2\text{H}$ .

This investigation of the properties of the  $\Delta^{\alpha}$ -oleic acid and its derivatives is somewhat incomplete, but the appearance of a paper by Ponzio (*loc. cit.*) on the same subject necessitates the publication of the results so far obtained. Having now obtained some knowledge of the properties of this class of higher unsaturated acids, the author intends to conclude his investigation of the action of dimethylaniline and quinoline on the  $\alpha$ -bromo-derivatives of the higher fatty acids.

#### EXPERIMENTAL.

*Preparation of  $\Delta^{\alpha}$ -Oleic Acid.*—Fifty grams of pure  $\alpha$ -bromostearic acid were added to 120 c.c. of 30 per cent. alcoholic potash, and the whole boiled for  $2\frac{1}{2}$  hours; the alcohol was then evaporated, the residue diluted with water, and after acidifying with dilute sulphuric acid, was extracted with ether. The ethereal solution was washed with water, dried with calcium chloride, and evaporated, when 41 grams of solid residue were obtained, which, on crystallisation from light petroleum, gave 13 grams of  $\alpha$ -hydroxystearic acid. The mother liquor from the  $\alpha$ -hydroxystearic acid was evaporated to dryness and fractionally crystallised first from ethyl acetate, and then from light petroleum, when 5 grams of pure  $\Delta^{\alpha}$ -oleic acid were obtained. The amount actually formed is no doubt much greater than this, and the low yield (12.9 per cent.) is due to the great difficulty experienced in isolating it from the mixture, and in all cases fractions are obtained which it is almost impossible to obtain in a crystalline condition. In one experiment, the acid was added to the boiling alcoholic solution, but the yield was not materially increased.

0.1358 gave 0.3820  $\text{CO}_2$  and 0.1492  $\text{H}_2\text{O}$ . C = 76.71; H = 12.20.

0.1496 „ 0.4206  $\text{CO}_2$  „ 0.1652  $\text{H}_2\text{O}$ . C = 76.67; H = 12.26.

$\text{C}_{18}\text{H}_{34}\text{O}_2$  requires C = 76.60; H = 12.06 per cent.

$\Delta^{\alpha}$ -Oleic Acid is readily soluble in ether, chloroform, or benzene in the cold, not readily soluble in cold alcohol, ethyl acetate, or acetone, and crystallises from light petroleum either in long, flat needles or glistering, square plates, melting at  $58-59^{\circ}$  and resolidifying at  $56-55^{\circ}$ . It reduces a cold alkaline solution of potassium permanganate, and is without action on a cold chloroform solution of bromine.

Its molecular weight was determined by titration with  $N/10$  sodium hydroxide solution, using phenolphthalein as indicator.

0.4946 required 17.57 c.c.  $N/10$  NaOH. M. W. = 281.5.

$\text{C}_{18}\text{H}_{34}\text{O}_2$  requires M. W. = 282.

The *silver* salt was obtained as a white precipitate on mixing warm alcoholic solutions of the sodium salt and silver nitrate.

0.1426 gave 0.2886  $\text{CO}_2$ , 0.1096  $\text{H}_2\text{O}$ , and 0.0398 Ag.

C = 55.20; H = 8.54; Ag = 27.91.

0.1520 gave 0.424 Ag. Ag = 27.89.

$\text{C}_{18}\text{H}_{33}\text{O}_2\text{Ag}$  requires C = 55.52; H = 8.48; Ag = 27.76 per cent.

The *lead* salt was obtained as a white, flocculent precipitate on mixing hot alcoholic solutions of the sodium salt and lead acetate; it is practically insoluble in ether and fuses at  $157^\circ$ .

0.1510 gave 0.0596  $\text{PbSO}_4$ . Pb = 26.96.

$(\text{C}_{18}\text{H}_{33}\text{O}_2)_2\text{Pb}$  requires Pb = 26.92 per cent.

The *ethyl* ester, prepared in the usual manner from the silver salt and ethyl iodide, is a white, waxy solid melting at  $25-26^\circ$ ; it is readily soluble in light petroleum, ethyl alcohol, ether, or acetone, and crystallises from methyl alcohol in glistening, flat needles.

0.1856 gave 0.5244  $\text{CO}_2$  and 0.2030  $\text{H}_2\text{O}$ . C = 77.06; H = 12.15.

$\text{C}_{20}\text{H}_{38}\text{O}_2$  requires C = 77.42; H = 12.26 per cent.

The acid is readily regenerated by hydrolysis of the ester with alcoholic potash.

The molecular weight of the ethyl ester was determined by the freezing point method, using benzene as a solvent.

0.484 in 20.444 benzene gave  $\Delta t - 0.386^\circ$ . M. W. = 301.

0.8132 „ 20.444 „ „  $\Delta t - 0.655^\circ$ . M. W. = 298.

$\text{C}_{20}\text{H}_{38}\text{O}_2$  requires M. W. = 310.

#### *Oxidation of $\Delta^a$ -Oleic Acid.*

*Production of Palmitic Acid.*—Three grams of the pure  $\Delta^a$ -oleic acid were mixed with 150 c.c. of water and potassium hydroxide added until the resulting solution was faintly alkaline. A  $1\frac{1}{2}$  per cent. solution of potassium permanganate was added to the cold solution, when an immediate reduction took place; the solution was finally heated in the water-bath, and the addition of the permanganate solution continued until it was no longer reduced. The resulting product was acidified with dilute sulphuric acid, and the manganese dioxide dissolved by means of sulphurous acid. The precipitated acid was extracted with ether, the ethereal solution washed, dried, and evaporated, and the residue crystallised from dilute alcohol, and finally from light petroleum, when an acid melting at  $62^\circ$  was obtained. It had all the properties of palmitic acid (m. p.  $62^\circ$ ), and did not depress the melting point of this substance.

0.1524 gave 0.4170  $\text{CO}_2$  and 0.1730  $\text{H}_2\text{O}$ .  $\text{C} = 74.63$ ;  $\text{H} = 12.61$ .

$\text{C}_{16}\text{H}_{32}\text{O}_2$  requires  $\text{C} = 75.00$ ;  $\text{H} = 12.50$  per cent.

*Production of  $\alpha\beta$ -Dihydroxystearic Acid.*—Two grams of pure  $\Delta^a$ -oleic acid were dissolved in 200 c.c. of water containing sufficient potassium hydroxide to leave the solution faintly alkaline; the whole was then well stirred by means of a turbine, and maintained at  $0^\circ$  throughout the operation. A 1 per cent. solution of potassium permanganate previously cooled to  $0^\circ$  was then very gradually added until a little more than the calculated quantity had been introduced. The whole was allowed to remain at  $0^\circ$  for about 20 minutes, then acidified with dilute sulphuric acid, and the manganese dioxide dissolved by means of sulphurous acid. The precipitated acid was extracted with ether, the ethereal solution washed, dried, and evaporated, and the residue crystallised from ethyl acetate until its melting point was constant.

0.1196 gave 0.3000  $\text{CO}_2$  and 0.1234  $\text{H}_2\text{O}$ .  $\text{C} = 68.41$ ;  $\text{H} = 11.46$ .

$\text{C}_{18}\text{H}_{36}\text{O}_4$  requires  $\text{C} = 68.35$ ;  $\text{H} = 11.39$  per cent.

*$\alpha\beta$ -Dihydroxystearic acid* is only slightly soluble in alcohol, ether, or acetone in the cold, and in hot chloroform or light petroleum, and crystallises from ethyl acetate in clusters of slender needles melting at  $126^\circ$  and resolidifying at  $124$ – $123^\circ$ ; it is appreciably soluble in boiling water.

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## CLXXIV.—*The Affinity Constants of Aniline and its Derivatives.*

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IN a previous paper by one of the present authors (Farmer, Trans., 1901, 79, 863) it was shown that the hydrolysis of salts of weak acids with strong bases could be determined by the partial extraction of the weak acid from the aqueous solution by means of benzene. The same method has now been applied to the salts of weak bases with strong acids.

Our present knowledge as to the dissociation constants of aniline derivatives depends on determinations of the hydrolysis of their salts by the catalysis of esters (Walker, *Zeit. physikal. Chem.*, 1889, 4, 319),

by the inversion of cane sugar (Bruner, *Wszechswiat*, 1893, 23, 365, compare *Zeit. physikal. Chem.*, 1900, 32, 133; Walker and Aston, *Trans.*, 1895, 67, 576), and by conductivity methods (Walker, *Zeit. physikal. Chem.*, 1889, 4, 333; Bredig, *ibid.*, 1894, 13, 289). The solubility determinations of Löwenherz (*Zeit. physikal. Chem.*, 1898, 25, 385) depend on the same principle, since they necessitate a knowledge of the dissociation constant of water. The strengths of these bases are too low for the direct determination of their electrical conductivities in aqueous solution by the ordinary methods. Thus, the value found by Bredig (*Zeit. physikal. Chem.*, 1893, 11, 829) for the affinity constant of aniline was much too high, as shown by the degree of hydrolysis of its salts. The majority of the derivatives of aniline are still weaker, and the direct conductivity method is thus quite inapplicable to their investigation.

The distribution method has been found to be very suitable for the examination of aniline derivatives. The methods employed were essentially the same as originally used for weak acids; the application of the method to weak bases is, however, experimentally simpler, in so far as the presence of traces of carbonic acid in the water has no appreciable disturbing effect, and thus the precautions necessary on this account in dealing with the salts of weak acids become superfluous.

One of the main advantages of the method is its applicability to many acids or bases which are sparingly soluble in water, and the investigation of which by other means is therefore excluded. This was previously illustrated by determinations made on hydroxyazo-benzene, and is further shown by a number of sparingly soluble aniline derivatives in the present paper.

It has been pointed out by Wood (*Trans.*, 1903, 83, 576) that when catalytic methods are employed, the determination of the dissociation constants of weak bases from the hydrolysis becomes very inaccurate when the hydrolysis exceeds about 95 per cent. It will be shown that the present method to a great extent overcomes this difficulty, for by the use of excess of free acid the accuracy of the determinations can be greatly increased. This may be illustrated by the values found for *p*-nitroaniline hydrochloride at different dilutions:

Dilution in litres.....	144	233	274	380
Hydrolysis found (per cent.).....	94.2	95.8	96.3	97.2
„ calculated from dilution formula.....	93.6	95.9	96.5	97.4

The applicability of the process at low temperatures offers a further advantage over the catalytic methods.

Experiment showed that the most suitable solvents for the extraction

of the inert bases from the water are benzene and carbon tetrachloride. Most other easily accessible solvents have disadvantages, owing either to partial solubility in water, too great volatility, or the possibility of their reacting with the substances under investigation. Solvents which undergo any decomposition on keeping are unsuitable for this purpose.

In the following experiments, benzene was used throughout. It was in most cases found convenient to use 1000 c.c. of water and 60 c.c. of benzene, 50 c.c. of the solvent being afterwards taken for the determination of the dissolved amine. In most instances, the amount of free base dissolved in the benzene was estimated gravimetrically, the benzene being distilled off at about  $40^{\circ}$  in a slow current of air, and the last traces removed in a vacuum desiccator. In the case of liquid amines, the hydrochloride was precipitated from the benzene by dry hydrogen chloride and determined gravimetrically, preliminary experiments having shown that aniline could be quantitatively recovered in this way. In order to determine the loss of benzene due to its solubility in water and to evaporation during the experiment, blank experiments were carried out, in which substances such as phenanthrene were employed. These passed completely into the benzene layer, and thus it was possible to calculate the volume of this layer after the experiment. On carrying out determinations under the same conditions as employed in the estimation of the hydrolysis, the total loss of benzene during the experiment was found to amount to 1.0 c.c., as a mean of four experiments. The calculations have therefore been made on the assumption that the volume of the benzene was 59.0 c.c., instead of 60.0 c.c. as originally taken. Experiments with chloroform showed that the loss by evaporation was much greater and not sufficiently constant to admit of the use of this solvent unless special precautions were taken.

In certain exceptional cases, the bases are too sparingly soluble in benzene to admit of the application of the method. This behaviour is shown chiefly by amphoteric electrolytes, doubtless owing to the formation of internal salts. Of those examined, *o*-aminobenzoic acid was the only one which was sufficiently soluble to admit of accurate measurements. Apart from these amphoteric compounds, however, the method is applicable to almost all organic bases.

The same notation is employed here as in the previous paper, with the slight modifications necessary for the application to weak bases instead of weak acids, namely :

$c_1$  = original concentration of hydrochloric acid.

$c_2$  = " " of weak base.

$c$  = concentration of free base in the aqueous layer.

$F$  = coefficient of distribution of the base between benzene and water.

$q$  = volume of benzene employed, per litre of water.

As previously shown, the percentage hydrolysis is then calculated by the following formulæ:

$$Km_4 = \frac{c[c_1 - c_2 + c(1 + qF)]}{c_2 - c(1 + qF)} \dots \dots \dots (i),$$

$$m_1^2 = Km_4(c_2 - m_1) \dots \dots \dots (ii),$$

$$\text{Percentage hydrolysis} = 100m_1/c_2 \dots \dots \dots (iii).$$

If the pure hydrochloride is taken without any excess of hydrochloric acid,  $c_2$  becomes equal to  $c_1$ , and equation (i) may be written:

$$Km_4 = \frac{c^2(1 + qF)}{c_2 - c(1 + qF)}.$$

It was first necessary to determine the ratios of distribution of the amines between benzene and water. For this purpose, a known quantity of the base was shaken with 1000 c.c. of water and 60 c.c. of benzene at  $25^\circ$ , and the amount of substance determined in 50 c.c. of the benzene solution, after filtration. Wherever possible, the amount remaining in the water was found by difference, but if the coefficient was very high, a second extraction of the water was carried out at the same temperature.

As is well known, the ratio of distribution of a number of substances (including some amines) between two solvents varies with the concentration, owing to association, hydration, or other disturbing factors. For this reason, it was necessary to carry out determinations at a number of different dilutions. In most instances, the concentration was found to exert a slight influence, but in general this could be neglected. In one case, however, namely, that of *o*-aminobenzoic acid, the association of the molecules in benzene solution rendered it necessary to ascertain by interpolation the ratio of distribution at each required dilution.

The coefficient of distribution having thus been found, the hydrolysis is determined by shaking a solution of the hydrochloride with benzene in the same manner, and measuring the quantity of base extracted from the aqueous solution.

## EXPERIMENTAL.

*Aniline and the Toluidines.**Ratio of distribution between benzene and water. Temperature = 25°.*

Base.	Weight of hydrochloride from 50 c.c. benzene.	Weight of base in 1000 c.c. water.	Ratio of distribu- tion of base.
Aniline .....	0·0914	0·1351	9·7
	0·0893	0·1222	10·5
	0·0457	0·0647	10·1
			10·1
<i>o</i> -Toluidine .....	0·1010	0·1124	13·4
	0·0594	0·0659	13·4
			13·4
<i>m</i> -Toluidine .....	0·1262	0·0990	19·0
	0·0710	0·0551	19·2
			19·1
<i>p</i> -Toluidine .....	0·1465	0·0923	23·6
	0·0695	0·0421	24·6
			24·1

*Hydrolysis of hydrochlorides. Temperature = 25°.*

Vol. of water = 1000 c.c. Vol. of benzene (corr.) = 59 c.c.

Base.	Concentra- tion of acid taken <i>c</i> <sub>1</sub> .	Concentra- tion of base taken <i>c</i> <sub>2</sub> .	Weight of hydro- chloride from 50 c.c. benzene.	Concentra- tion of free base in water layer <i>c</i> .	Per- centage hydro- lysis.	Dilution in litres.
Aniline .....	0·09969	0·09969	0·0806	0·00123	1·56	10·0
F=10·1 ...	0·03138	0·03138	0·0406	0·000621	2·51	31·9
<i>o</i> -Toluidine ...	0·1009	0·1009	0·2741	0·00285	3·80	9·9
F=13·4 ...	0·03149	0·03149	0·1589	0·00165	7·12	31·8
<i>m</i> -Toluidine...	0·1002	0·1002	0·1793	0·00131	1·92	10·0
F=19·1 ...	0·03130	0·03130	0·1080	0·000783	3·69	32·0
<i>p</i> -Toluidine ...	0·09958	0·09958	0·1133	0·000655	1·02	10·0
F=24·1 ...	0·03128	0·03128	0·0622	0·000360	1·80	32·0

Previous measurements of the hydrolysis of certain amine hydrochlorides have been made by Bredig (*Zeit. physikal. Chem.*, 1894, 13, 289) by the electrical conductivity method. Löwenherz has also measured the strengths of some aniline derivatives by solubility determinations (*Zeit. physikal. Chem.*, 1898, 25, 385). A comparison may be drawn between the results of the three methods for aniline hydrochloride, the hydrolysis being calculated in each instance for a dilution of 32 litres.

Electrical method (Bredig) .....	hydrolysis = 2.76 per cent.
Solubility determinations (Löwenherz)...	„ = 2.67 „
Distribution method (from the mean constant) .....	„ = 2.65 „

For the toluidines the deviations are somewhat greater, but the order of their strengths is the same.

The sulphates of these bases were examined in order to throw light on an anomaly which has been found in the hydrolysis of inorganic sulphates. It has been shown by Ley (*Zeit. physikal. Chem.*, 1899, 30, 218), by means of the velocity of inversion of cane sugar, that ferric and aluminium sulphates are less hydrolysed than the corresponding chlorides. Similar observations have been made by Bruner (*Zeit. physikal. Chem.*, 1900, 32, 133), Long (*J. Amer. Chem. Soc.*, 1896, 18, 693), and Kahlenberg, Davis, and Fowler (*ibid.*, 1899, 21, 1) by the same method, and confirmed by Carrara and Vespignani by the method of ester catalysis (*Gazzetta*, 1900, 30, ii, 35). This result is surprising, for we should expect that sulphuric acid, being a weaker acid than hydrochloric, should be expelled from its salts to a greater extent than the latter. Since the hydrolysis of the salts of polyvalent metals such as iron and aluminium probably takes place in several stages, it appeared desirable to repeat the experiments with monacid bases. The results of these experiments show that the sulphates of aniline and the toluidines do not exhibit this abnormal behaviour. It is difficult at present to account for the abnormalities in the hydrolysis of the above metallic sulphates.

*Hydrolysis of sulphates of aniline and toluidines.* Temperature = 25°.

Vol. of water = 1000 c.c. Vol. of benzene (corr.) = 59 c.c.

Salt.	Concentra- tion of acid taken $c_1$ .	Concentra- tion of base taken $c_2$ .	Weight of hydro- chloride from 50 c.c. benzene.	Concentra- tion of free base in water layer $c$ .	Per- centage hydro- lysis.	Dilution in litres.
Aniline sulphate...	0.10520	0.10440	0.1106	0.00169	2.34	9.6
	0.09134	0.09134	0.1204	0.00184	2.55	10.9
	0.03281	0.03257	0.0548	0.000838	3.48	30.7
	0.03120	0.03120	0.0595	0.000910	3.70	32.1
<i>o</i> -Toluidine sulphate	0.10520	0.09963	0.2383	0.00248	4.96	10.0
	0.15220	0.07610	0.0190	0.000198	4.98	13.1
	0.03290	0.03137	0.1360	0.00142	7.68	31.9
	0.04767	0.02383	0.0158	0.000164	8.07	42.0
<i>m</i> -Toluidine sulphate	0.1000	0.1000	0.2928	0.00214	3.12	10.0
	0.03130	0.03130	0.1248	0.000911	4.32	32.0
<i>p</i> -Toluidine sulphate	0.1000	0.1000	0.1576	0.000911	1.43	10.0
	0.03132	0.03132	0.0768	0.000444	2.22	32.0

The following comparison between the hydrochlorides and sulphates of these bases shows that the hydrolysis is greater throughout in the case of the sulphates. The relative difference between the hydrochlorides and sulphates is greater at the higher concentration, as was to be expected from the influence of the concentration on the ionisation of the sulphuric acid.

*Hydrolysis of hydrochlorides and sulphates of amines.*

Temperature = 25°.

	Hydrochloride.		Sulphate.	
	N/10.	N/32.	N/10.	N/32.
Aniline.....	1·56	2·51	2·40	3·70
<i>o</i> -Toluidine.....	3·80	7·12	4·96	7·68
<i>m</i> -Toluidine.....	1·92	3·69	3·12	4·32
<i>p</i> -Toluidine.....	1·02	1·80	1·43	2·22

In the case of the following derivatives of aniline, the amount of free base dissolved in the benzene was determined directly by evaporating the solution as described above and weighing the residue.

*Ratios of distribution between benzene and water.* Temperature = 25°.

Base.	Weight of base in 50 c.c. benzene.	Weight of base in 1000 c.c. water.	Ratio of distribution.
<i>o</i> -Nitroaniline .....	0·8385	0·2580	65·0
	0·9450	0·2910	65·0
	0·4110	0·1325	62·0
			64·0
<i>m</i> -Nitroaniline .....	0·5855	0·4800	24·4
	0·3400	0·2975	22·9
	0·3325	0·2960	22·5
			23·3
<i>p</i> -Nitroaniline .....	0·2020	0·4365	9·3
	0·1295	0·2920	8·9
	0·0780	0·1795	8·7
			9·0
<i>p</i> -Chloroaniline.....	0·7160	0·1769	81
	1·0510	0·2548	82
	1·4180	0·3271	87
			83
<i>p</i> -Bromoaniline.....	1·0620	0·1579	135
	1·3465	0·2089	129
			132
<i>p</i> -Anisidine .....	0·2178	0·7468	5·9
	0·3331	1·1118	6·0
	0·4505	1·4722	6·1

6·0

*Ratios of distribution between benzene and water. Temperature = 25°*  
(continued).

Base.	Weight of base in 50 c.c. benzene.	Weight of base in 1000 c.c. water.	Ratio of distribution.
<i>p</i> -Nitrosomethylaniline...	0.0457	0.2791	3.27
	0.0462	0.2785	3.31
	0.0270	0.1679	3.22
			3.27
<i>p</i> -Nitrosodimethylaniline	0.6900	0.2630	52.5
	0.5678	0.2263	50.1
			51.3
<i>o</i> -Phenylenediamine.....	0.0273	0.9818	0.556
	0.2040	7.5470	0.541
			0.549
<i>m</i> -Phenylenediamine.....	0.0828	9.0880	0.182
	0.0463	5.2600	0.176
			0.179
Acetanilide .....	0.2925	3.538	1.654
	0.2926	3.537	1.656
	0.2918	3.539	1.650
			1.653
Aceto- <i>o</i> -toluidide .....	0.2883	3.845	1.500
	0.2939	3.838	1.531
			1.516
$\alpha$ -Naphthylamine .....	0.7820	0.0664	235
	1.1815	0.0926	255
	1.5855	0.1186	267
			252
$\beta$ -Naphthylamine .....	0.7970	0.0566	281
	0.8705	0.0664	262
	1.2705	0.0862	294
			279
Aminoazobenzene .....	1.4180	0.0089	3180
	1.4315	0.0089	3210
	1.8330	0.0117	3130
			3170
<i>o</i> -Aminobenzoic acid.....	0.0203	0.7709	0.54
	0.0325	0.9595	0.68
	0.0950	1.9690	0.96
	0.1250	2.3000	1.09
	0.1732	2.7878	1.24

In the following determinations of the hydrolysis, the hydrochloric acid was in general assumed to be completely ionised, but in the case

of acetanilide and aceto-*o*-toluidide, where a large excess of acid was used, a small correction was necessary for the incompleteness of the ionisation.

*Hydrolysis of hydrochlorides.* Temperature = 25°.

*p*-Chloroaniline. F = 83. Vol. of water = 1000 c.c. Vol. of benzene (corr.) = 59 c.c.

Concentration of acid taken $c_1$ .	Concentration of base taken $c_2$ .	Weight of base from 50 c.c. benzene.	Concentration of free base in water layer c.	Percentage hydrolysis.	Dilution in litres.
0.03663	0.03316	0.2300	0.0004347	4.94	30.2
0.02745	0.02485	0.2075	0.0003921	5.70	40.2
0.01841	0.01665	0.1776	0.0003356	6.91	60.1

*p*-Bromoaniline. F = 132. Vol. of water = 1000 c.c. Vol. of benzene (corr.) = 59 c.c.

0.03440	0.03144	0.5084	0.0004479	5.82	31.8
0.02597	0.02322	0.4213	0.0003711	6.70	43.1
0.01733	0.01559	0.3699	0.0003258	8.34	64.1

*p*-Anisidine. F = 6.0. Vol. of water = 1000 c.c. Vol. of benzene (corr.) = 59 c.c.

0.06087	0.06087	0.0223	0.000604	1.15	16.4
0.04673	0.04673	0.0200	0.000542	1.35	21.4
0.03914	0.03914	0.0170	0.000461	1.37	25.6

*p*-Nitrosomethylaniline. F = 3.27. Vol. of water = 100 c.c. Vol. of benzene (corr.) = 60 c.c.

0.03950	0.03874	0.0184	0.000828	4.25	25.8
0.03302	0.03228	0.0160	0.000720	4.50	31.0
0.02654	0.02582	0.0150	0.000675	5.31	38.7

*p*-Nitrosodimethylaniline. F = 51.3. Vol. of water = 1000 c.c. Vol. of benzene (corr.) = 59 c.c.

0.01984	0.01199	0.0333	0.0000864	6.87	83.4
0.01681	0.00931	0.0265	0.0000689	7.68	107.4
0.01520	0.00664	0.0178	0.0000461	9.24	150.6

$\alpha$ -Naphthylamine. F = 252. Vol. of water = 1000 c.c. Vol. of benzene (corr.) = 59 c.c.

0.03387	0.03135	0.6531	0.0003625	5.93	31.9
0.02571	0.02346	0.5558	0.0003085	6.86	42.6
0.01714	0.01568	0.4626	0.0002567	8.48	63.8

$\beta$ -Naphthylamine. F = 279. Vol. of water = 1000 c.c. Vol. of benzene (corr.) = 59 c.c.

0.03374	0.03127	0.4752	0.0002382	4.22	32.0
0.02588	0.02354	0.3935	0.0001973	4.80	42.5
0.01803	0.01564	0.3084	0.0001546	6.04	63.9

*Hydrolysis of hydrochlorides. Temperature = 25° (continued).*

*Aminoazobenzene.*  $F = 3170$ . Vol. of water = 1000 c.c. Vol. of benzene (corr.) = 59 c.c.

Concentration of acid taken $c_1$ .	Concentration of base taken $c_2$ .	Weight of base from 50 c.c. benzene.	Concentration of free base in water layer c.	Percentage hydrolysis.	Dilution in litres.
0.03204	0.01522	2.2163	0.0000710	23.8	65.7
0.03459	0.01069	1.5652	0.0000501	29.4	93.5
0.02793	0.00855	1.2789	0.0000410	32.2	116.9

*Acetanilide.*  $F = 1.653$ . Vol. of water = 1000 c.c. Vol. of benzene (corr.) = 59 c.c.

0.3280	0.02880	0.2901	0.02600	99.90	34.7
0.3280	0.02880	0.2874	0.02576	99.80	34.7
0.3280	0.02880	0.2870	0.02572	99.79	34.7

*Aceto-o-toluidide.*  $F = 1.516$ . Vol. of water = 1000 c.c. Vol. of benzene (corr.) = 59 c.c.

0.3260	0.02808	0.2846	0.02520	99.74	35.6
0.3260	0.02808	0.2825	0.02501	99.68	35.6
0.3260	0.02808	0.2844	0.02518	99.74	35.6

*o-Phenylenediamine.*  $F = 0.549$ . Vol. of water = 100 c.c. Vol. of benzene (corr.) = 59 c.c.

0.1341	0.1341	0.0056	0.00189	1.6	7.5
0.1341	0.1341	0.0055	0.00186	1.6	7.5

Experiments with *m*- and *p*-phenylenediamines are not included, as the very low ratios of distribution of the bases between benzene and water rendered the results somewhat uncertain. For the same reason, experiments on *m*- and *p*-aminobenzoic acids were discontinued. In determining the hydrolysis of the hydrochloride of *o*-aminobenzoic acid, it was necessary to ascertain the ratio of distribution at each dilution by interpolation, since the aminobenzoic acid was partially associated to double molecules in benzene solution.

*Hydrolysis of the hydrochloride of o-aminobenzoic acid. Temp. = 25°.*

Vol. of water = 1000 c.c. Vol. of benzene (corr.) = 59 c.c.

Concentration of acid taken $c_1$ .	Concentration of base taken $c_2$ .	Weight of base from 50 c.c. benzene.	Ratio of distribution.	Percentage hydrolysis.	Dilution in litres.
0.07500	0.07445	0.1605	1.20	27.6	13.4
0.05000	0.04995	0.1132	1.04	33.0	20.0
0.05000	0.04991	0.1139	1.04	33.3	20.0
0.05010	0.02503	0.0220	0.55	45.5	40.0

On applying the "dilution-law" to the above results, it is found that the deviations from the theoretical values are very slight, thus showing that the accuracy of the method is not lessened by the above interpolation. Previous determinations of the hydrolysis of *o*-amino-benzoic acid hydrochloride by the catalysis of esters (Winkelblech, *Zeit. physikal. Chem.*, 1901, **36**, 546) agree closely with the foregoing values, but results obtained by this author with the conductivity method do not show the same concordance. The results at 25°, recalculated in each case to the dilution  $v_{32}$ , are as follows :

Distribution method.....	hydrolysis = 40 l per cent.
Ester catalysis (Winkelblech).....	„ = 41.1 „
Electrical conductivity „ .....	„ = [35.5] „

Measurements on the hydrochlorides of the nitroanilines showed that the ortho-derivative is so much weaker than the meta- and para-isomerides that its slight salt formation could only be detected in presence of a considerable excess of hydrochloric acid. A correction has been applied for the incompleteness of the ionisation of the acid.

*Nitroaniline hydrochlorides.* Temperature = 25°.

Vol. of water = 1000 c.c. Vol. of benzene (corr.) = 59 c.c.

Concen- tration of acid taken $c_1$ .	Concen- tration of base taken $c_2$ .	Weight of base from 50 c.c. benzene.	Concentration of free base in water layer c.	Percentage hydrolysis.	Dilution in litres.
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*o*-Nitroaniline.  $F = 64.0$ .

0.20140	0.00770	0.7020	0.001590	99.71	130
0.20140	0.00448	0.4055	0.000918	99.73	223

*m*-Nitroaniline.  $F = 23.3$ .

0.05035	0.02142	0.2610	0.001623	31.2	46.7
0.02518	0.01014	0.2005	0.001247	42.2	98.6
0.05035	0.00777	0.0715	0.000445	45.1	128.7

*p*-Nitroaniline.  $F = 9.0$ .

0.05035	0.00693	0.2165	0.003468	94.2	144
0.02518	0.00430	0.1495	0.002407	95.8	233
0.05035	0.00366	0.1095	0.001763	96.3	274
0.02518	0.00263	0.0900	0.001450	97.2	330

The extreme weakness of *o*-nitroaniline as a base is noteworthy. Evidently the close proximity of the nitro-group has almost nullified the basic properties of the amino-group. Walker, indeed, found (*Zeit. physikal. Chem.*, 1889, **4**, 319) that a solution of *o*-nitroaniline

hydrochloride conducted better than hydrochloric acid, and concluded from this that the nitroaniline possessed acid properties. In support of this, he found that *o*-nitroaniline had a measurable electrical conductivity in aqueous solution. In order to examine this point further, the salt formation of the three nitroanilines with potassium hydroxide has been measured by the distribution method. A large excess of the alkali was taken, and allowance has therefore been made for the incompleteness of its dissociation.

*Nitroanilines in alkaline solution.* Temperature = 25°.

Vol. of water = 1000 c.c. Vol. of benzene (corr.) = 59 c.c.

Substance.	Dilution in litres.	Concentration of nitroaniline.	Concentration of potassium hydroxide.	Weight of nitroaniline from 50 c.c. benzene.	Salt formation per cent.
<i>o</i> -Nitroaniline...	122	0.008225	0.38500	0.7805	-0.31
<i>m</i> - " ...	121	0.008261	0.38500	0.5855	-0.27
<i>p</i> - " ...	222	0.004507	0.38500	0.1953	-0.13

These results show that no formation of salt occurs, and hence that the nitroanilines have no acid properties. The values are slightly negative owing to the property which alkalis have of suppressing the solubility of weak bases (compare Sackur, *Ber.*, 1902, 35, 1245).

Experiments were also carried out on *p*-nitrosomono- and -di-methylanilines in alkaline solution. Since these compounds are somewhat easily decomposed into nitrosophenol in alkaline solution, the experiments were carried out at a lower temperature.

*Ratio of distribution between benzene and water.* Temperature = 6°.

Substance.	Weight of base in 50 c.c. benzene.	Weight of base in 1000 c.c. water.	Ratio of Distribution.
<i>p</i> -Nitrosomethylaniline ...	0.1930	1.236	3.12
	0.1918	1.250	3.07
	0.1499	1.043	2.87
			3.02
<i>p</i> -Nitrosodimethylaniline...	0.2755	0.1473	37.5
	0.2296	0.1228	37.3
	0.1829	0.0992	37.0
			37.3

*p*-Nitrosomethylaniline and *p*-nitrosodimethylaniline in alkaline solution.  
Temperature = 6°.

Dilution in litres.	Concen- tration of amine.	Concen- tration of baryta.	Weight of amine from 50 c.c. benzene.	Hydro- lysis of barium salt.	Salt formation per cent.
<i>p</i> -Nitrosomethylaniline. F = 3.02. Vol. of water = 100 c.c. Vol. of benzene (corr.) = 62 c.c.					

47.2	0.02118	0.02187	0.1166	60.3	39.7
70.8	0.01412	0.01459	0.0834	67.5	32.5

<i>p</i> -Nitrosodimethylaniline. F = 37.3. Vol. of water = 1000 c.c. Vol. of benzene (corr.) = 64 c.c.					
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457	0.002189	0.004367	0.1837	102.8	—
685	0.001459	0.002923	0.1218	101.9	—

*p*-Nitrosomethylaniline shows, therefore, distinctly acid properties. If the dissociation of water at 6° be taken as  $4.7 \times 10^{-8}$ , the affinity constant of *p*-nitrosomethylaniline, as an acid, is  $1.12 \times 10^{-13}$ . The dimethyl compound, on the other hand, behaves only as a base, showing that a hydrogen atom in direct combination with the nitrogen is necessary for the existence of acid properties. The direct introduction of an alkali metal into the amino-group appears improbable; a transformation of the nitrosomethylaniline to a compound of the quinone type (compare Lloyd, *Dissert. Würzburg*, 1903) being much more likely.

*Summary of Results.*

In the following table the hydrolysis of the above hydrochlorides has been recalculated in every case to the same dilution, with the help of the dilution-law, the mean constant being taken for this purpose. The affinity constants of the free bases have also been calculated, assuming the degree of dissociation of pure water at 25° to be  $1.09 \times 10^{-7}$ .

*Comparison of the strengths of weak bases.* Temperature = 25°.

Base.	Ratio of distribution between benzene and water.	Percentage hydrolysis of hydrochloride at $v_{32}$ .	$\frac{x^2}{(1-x)v}$ (mean).	Affinity constant of free base.
Aniline .....	10.1	2.7	$2.25 \times 10^{-5}$	$5.3 \times 10^{-10}$
<i>o</i> -Toluidine .....	13.4	7.0	$1.62 \times 10^{-4}$	$7.3 \times 10^{-11}$
<i>m</i> - " .....	19.1	3.6	$4.10 \times 10^{-5}$	$2.9 \times 10^{-10}$
<i>p</i> - " .....	24.1	1.8	$1.05 \times 10^{-5}$	$1.13 \times 10^{-9}$
<i>o</i> -Nitroaniline .....	64.0	98.6	2.1	$5.6 \times 10^{-15}$
<i>m</i> - " .....	23.3	26.6	$3.01 \times 10^{-3}$	$4.0 \times 10^{-12}$
<i>p</i> - " .....	9.0	79.6	$9.58 \times 10^{-2}$	$1.24 \times 10^{-13}$
<i>p</i> -Chloroaniline .....	83	5.1	$8.56 \times 10^{-5}$	$1.49 \times 10^{-10}$
<i>p</i> -Bromoaniline .....	132	5.9	$1.14 \times 10^{-4}$	$1.04 \times 10^{-10}$
<i>p</i> -Anisidine .....	6.0	1.6	$8.08 \times 10^{-6}$	$1.47 \times 10^{-9}$
<i>p</i> -Nitrosomethylaniline ...	3.27	4.7	$7.29 \times 10^{-5}$	$1.63 \times 10^{-10}$
<i>p</i> -Nitrosodimethylaniline .	51.3	4.3	$6.09 \times 10^{-5}$	$1.95 \times 10^{-10}$
<i>o</i> -Aminobenzoic acid .....	—	40.1	$8.45 \times 10^{-3}$	$1.41 \times 10^{-12}$
<i>o</i> -Phenylenediamine .....	0.549	3.3	$3.60 \times 10^{-5}$	$3.3 \times 10^{-10}$
Acetanilide .....	1.653	99.8	[19]	—
Aceto- <i>o</i> -toluidide .....	1.516	99.7	[11]	—
$\alpha$ -Naphthylamine .....	252	6.0	$1.20 \times 10^{-4}$	$9.9 \times 10^{-11}$
$\beta$ -Naphthylamine .....	279	4.2	$5.83 \times 10^{-5}$	$2.0 \times 10^{-10}$
Aminozobenzene .....	3170	18.1	$1.25 \times 10^{-3}$	$9.5 \times 10^{-12}$

UNIVERSITY, BIRMINGHAM.

# CLXXV.—*The Formation and Reactions of Imino-compounds. Part I. Condensation of Ethyl Cyanoacetate with its Sodium Derivative.*

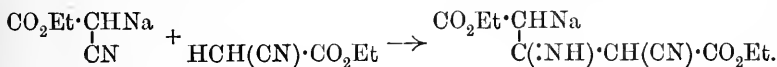
By HAROLD BARON, FREDERICK GEORGE PERCY REMFRY, and JOCELYN FIELD THORPE.

THIS work originated in a desire to obtain evidence of the existence of the sodium compound of ethyl cyanoacetate in an "enol" form, this substance having been shown by one of us to exhibit properties very different from the corresponding sodium derivative of ethyl malonate (Trans., 1900, 77, 923).

Baeyer (*Ber.*, 1885, 13, 3454), on treating ethyl malonate with an equivalent quantity of its sodium derivative in alcoholic solution, obtained ethyl phloroglucinoltricarboxylate, and concluded from this that the sodium atom in the sodium derivative was undoubtedly attached to carbon (see also Moore, this vol., p. 165).

On applying a similar reaction to ethyl cyanoacetate, it was at once apparent that the condensation between this substance and its sodium derivative proceeded in quite a different way.

After heating only a short time on the water-bath, a large quantity of a sodium compound was obtained, which ultimately proved to be the sodium derivative of ethyl  $\beta$ -imino- $\alpha$ -cyanoglutarate, the condensation evidently having proceeded according to the equation :

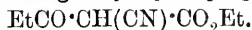


The proof of the constitution of this sodium compound is as follows.

With dilute mineral acids, it is converted into ethyl  $\beta$ -imino- $\alpha$ -cyanoglutarate,  $\text{CO}_2\text{Et} \cdot \text{CH}_2 \cdot \text{C}(\text{:NH}) \cdot \text{CH}(\text{CN}) \cdot \text{CO}_2\text{Et}$ , which, on boiling with dilute sodium carbonate solution, is transformed into ethyl hydrogen  $\beta$ -imino- $\alpha$ -cyanoglutarate,  $\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{C}(\text{:NH}) \cdot \text{CH}(\text{CN}) \cdot \text{CO}_2\text{Et}$ . On distilling the ammonium salt of this substance, it yields ethyl  $\beta$ -imino- $\alpha$ -cyanobutyrate,  $\text{MeC}(\text{:NH}) \cdot \text{CH}(\text{CN}) \cdot \text{CO}_2\text{Et}$ , which passes into ethyl cyanoacetoacetate,  $\text{MeCO} \cdot \text{CH}(\text{CN}) \cdot \text{CO}_2\text{Et}$ , on distillation with dilute sulphuric acid.

Ethyl cyanoacetoacetate prepared in this way is identical with the substance prepared by Haller and Held (*Ann. Chim. Phys.*, 1889, [vi], 17, 204) by the interaction of cyanogen chloride and ethyl acetoacetate, or by the condensation of acetyl chloride with ethyl sodio-cyanoacetate.

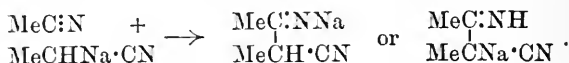
The position of the sodium atom in the sodium compound of ethyl  $\beta$ -imino- $\alpha$ -cyanoglutarate is shown by the following considerations. It reacts with methyl iodide to form ethyl  $\beta$ -imino- $\alpha$ -cyano- $\alpha'$ -methylglutarate,  $\text{CO}_2\text{Et} \cdot \text{CHMe} \cdot \text{C}(\text{:NH}) \cdot \text{CH}(\text{CN}) \cdot \text{CO}_2\text{Et}$ ; on hydrolysis with sodium carbonate, this substance yields ethyl hydrogen  $\beta$ -imino- $\alpha$ -cyano- $\alpha'$ -methylglutarate,  $\text{CO}_2\text{H} \cdot \text{CHMe} \cdot \text{C}(\text{:NH}) \cdot \text{CH}(\text{CN}) \cdot \text{CO}_2\text{Et}$ , the ammonium salt of which, on distillation, gives ethyl  $\beta$ -imino- $\alpha$ -cyanovalerate,  $\text{EtC}(\text{:NH}) \cdot \text{CH}(\text{CN}) \cdot \text{CO}_2\text{Et}$ , this in turn, when distilled with dilute sulphuric acid, yielding ethyl cyanopropionylacetate,



The final product is identical with that prepared by Haller (*Ber.*, 1888, 21, 354) by the interaction of ethyl sodiocyanoacetate and propionyl chloride.

In the same way, ethyl  $\beta$ -imino- $\alpha$ -cyano- $\alpha'$ -ethylglutarate,  $\text{CO}_2\text{Et} \cdot \text{CHEt} \cdot \text{C}(\text{:NH}) \cdot \text{CH}(\text{CN}) \cdot \text{CO}_2\text{Et}$ , prepared by the action of ethyl iodide on the sodium derivative, gives ethyl hydrogen  $\beta$ -imino- $\alpha$ -cyano- $\alpha'$ -ethylglutarate,  $\text{CO}_2\text{H} \cdot \text{CHEt} \cdot \text{C}(\text{:NH}) \cdot \text{CH}(\text{CN}) \cdot \text{CO}_2\text{Et}$ , ethyl  $\beta$ -imino- $\alpha$ -cyanocaproate,  $\text{Pr}^{\text{c}}\text{C}(\text{:NH}) \cdot \text{CH}(\text{CN}) \cdot \text{CO}_2\text{Et}$ , and ethyl  $n$ -butyrylcyanacetate,  $\text{Pr}^{\text{c}}\text{CO} \cdot \text{CH}(\text{CN}) \cdot \text{CO}_2\text{Et}$ , the latter being identical with the compound prepared by Haller from ethyl sodio-cyanoacetate and butyryl chloride.

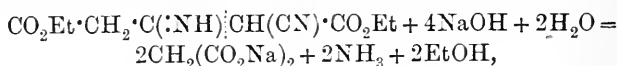
The formation of ethyl  $\beta$ -imino- $\alpha$ -cyanoglutarate in the foregoing condensation is evidently analogous to the production of the di-molecular nitriles which E. von Meyer (*J. pr. Chem.*, 1889, [ii], 39, 189) and Riess and E. von Meyer (*ibid.*, 1885, [ii], 31, 112) prepared by the action of sodium on a solution of the nitrile in dry ether. They represent this reaction as occurring in the following way :



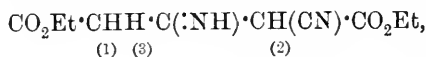
From our experiments, however, it would appear that the nitrile group of the sodium derivative passes into the imino-group in accordance with the equation given on the previous page.

The greatest yield of the condensation product is formed when the reacting substances are in the proportion of one molecule of ethyl cyanoacetate to one molecule of its sodium derivative. A greater or less amount of sodium than this proportionately diminishes the yield.

The similarity between the reactions of substances containing the groups C:NH and CO is clearly shown by the behaviour of ethyl  $\beta$ -imino- $\alpha$ -cyanoglutarate towards reagents. Thus with strong alkaline hydrolytic agents it is completely decomposed into the alkali salt of malonic acid in accordance with the equation :



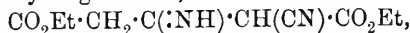
behaving therefore in the same way as would a compound having the formula  $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}$ . Again, the hydrogen atoms marked 1, 2, and 3 in ethyl  $\beta$ -imino- $\alpha$ -cyanoglutarate,



are replaceable by sodium in the order indicated by the numerals.

The proof of this is as follows :—

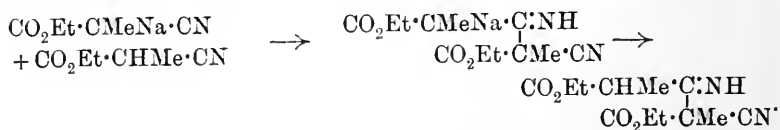
Ethyl  $\beta$ -imino- $\alpha$ -cyanoglutarate,



gives ethyl  $\beta$ -imino- $\alpha$ -cyano- $\alpha\alpha'$ -dimethylglutarate,



on treatment with sodium ethoxide and methyl iodide, and this substance is identical with the compound prepared by the condensation of ethyl cyanomethylacetate with its sodium derivative, which evidently takes place in accordance with the equation :



The sodium derivative, on direct treatment with methyl iodide, yields ethyl  $\beta$ -imino- $\alpha$ -cyano- $\alpha\alpha'$ -trimethylglutarate,



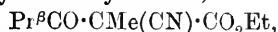
identical with the compound prepared by the complete methylation of ethyl  $\beta$ -imino- $\alpha$ -cyanoglutarate with sodium ethoxide and methyl iodide.

The constitution of these substances is further shown by the products they yield on hydrolysis; thus ethyl  $\beta$ -imino- $\alpha$ -cyano- $\alpha\alpha'$ -dimethylglutarate gives with sodium carbonate solution ethyl  $\beta$ -imino- $\alpha$ -cyano- $\alpha$ -methylvalerate,  $\text{EtC}(\text{:NH}) \cdot \text{CMe}(\text{CN}) \cdot \text{CO}_2\text{Et}$ , which, on distillation with dilute sulphuric acid, is converted into ethyl propionylcyanoacetate,  $\text{EtCO} \cdot \text{CMe}(\text{CN}) \cdot \text{CO}_2\text{Et}$ ; it also gives methylmalonic acid as sole product on complete hydrolysis with sodium hydroxide.

In the same way, ethyl  $\beta$ -imino- $\alpha$ -cyano- $\alpha\alpha'$ -trimethylglutarate yields ethyl  $\beta$ -imino- $\alpha$ -cyano- $\alpha$ -methylisobutyrylacetate,



and ethyl isobutyrylcyanomethylacetate,



and gives on complete hydrolysis with sodium hydroxide solution a mixture of methylmalonic and dimethylmalonic acids.

Compounds of the type  $\text{CO}_2\text{Et} \cdot \text{CH}_2 \cdot \text{C}(\text{:NH}) \cdot \text{CH}(\text{CN}) \cdot \text{CO}_2\text{Et}$  do not give colorations with ferric chloride, neither do they react with nitrous acid to form nitrosoamines, but yield oximes where the formulæ permit or otherwise remain unacted on. Thus the ethyl hydrogen salt,  $\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{C}(\text{:NH}) \cdot \text{CH}(\text{CN}) \cdot \text{CO}_2\text{Et}$ , gives with nitrous acid the oxime  $\text{HON}:\text{CH} \cdot \text{C}(\text{:NH}) \cdot \text{CH}(\text{CN}) \cdot \text{CO}_2\text{Et}$ , whereas the ethyl salt,  $\text{MeC}(\text{:NH}) \cdot \text{CH}(\text{CN}) \cdot \text{CO}_2\text{Et}$ , is, under ordinary conditions, unaffected.

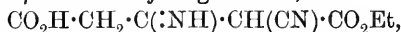
These oximes are well defined crystalline solids which give coloured salts with alkalis and are characterised by giving in neutral solution intense blue to green colorations with ferrous sulphate.

A comparison of ethyl  $\beta$ -imino- $\alpha$ -cyanobutyrate,



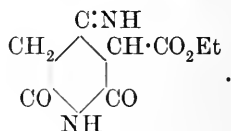
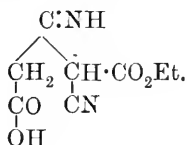
with ethyl cyanoacetoacetate,  $\text{MeCO} \cdot \text{CH}(\text{CN}) \cdot \text{CO}_2\text{Et}$ , shows that the substitution of NH for oxygen raises the boiling point of the compound about  $100^\circ$ . Thus the former substance boils at  $210^\circ/30$  mm., the latter at  $119^\circ/30$  mm.

Ethyl hydrogen  $\beta$ -imino- $\alpha$ -cyanoglutarate,

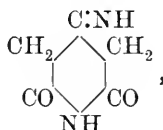


melts at  $142^\circ$  and at  $160^\circ$  gives off carbon dioxide, becoming converted into ethyl  $\beta$ -imino- $\alpha$ -cyanobutyrate. If, however, the ethyl hydrogen salt is kept one or two degrees above its melting point for ten minutes, it again becomes solid, being transformed into ethyl glutazincarboxylate. This conversion, which takes place when the hydrogen

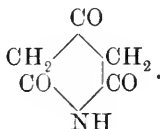
salt has been carefully dried, is evidently due to a molecular rearrangement:



The constitution of this substance is shown by its behaviour on hydrolysis; thus with sodium hydroxide solution it is converted into glutazine:



which, on boiling for a few minutes with concentrated hydrochloric acid, yields 2:4:6-trioxypyridine:



Ethyl glutazinecarboxylate is, however, best prepared by the action of cold concentrated sulphuric acid on ethyl  $\beta$ -imino- $\alpha$ -cyanoglutarate,  $\text{CO}_2\text{Et} \cdot \text{CH}_2 \cdot \text{C}(\text{:NH}) \cdot \text{CH}(\text{CN}) \cdot \text{CO}_2\text{Et}$ , under which conditions the conversion into the cyclic compound is quantitative. This method has been adopted in the case of the various alkylated derivatives of ethyl  $\beta$ -imino- $\alpha$ -cyanoglutarate, described in this communication, and in most cases a quantitative yield of the corresponding glutazine derivative has been obtained. In the same way, the various alkylated ethyl hydrogen salts of ethyl  $\beta$ -imino- $\alpha$ -cyanoglutarate of the type:



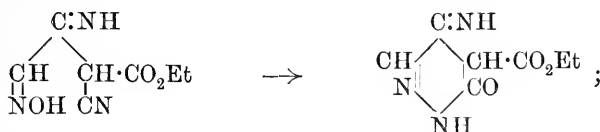
(where R = alkyl or hydrogen), give, on heating a few degrees above their melting points, the corresponding alkylated ethyl glutazinecarboxylate derivatives, which on hydrolysis with caustic alkali give the corresponding alkylated glutazines.

That other  $\gamma$ -cyano-acids undergo the same intermolecular change on heating, is shown by the similar behaviour of ethyl hydrogen cyanoacetonedicarboxylate,  $\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}(\text{CN}) \cdot \text{CO}_2\text{Et}$ , which is prepared by methods given in the experimental portion of this paper;

this acid, when heated a few degrees above its melting point, is transformed into ethyl 2 : 4 : 6-trioxypyridine-3-carboxylate :

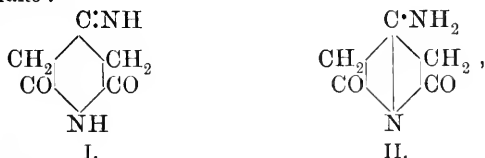


Another instance of the same kind of change is exhibited by the oxime,  $\text{CH}(\text{:NOH}) \cdot \text{C}(\text{:NH}) \cdot \text{CH}(\text{CN}) \cdot \text{CO}_2\text{Et}$ ; this substance melts, but instantly decomposes with separation of carbon. If, however, it is slowly added to concentrated sulphuric acid, it is transformed into a pyridazine derivative in accordance with the equation :



this and similar compounds are still under investigation.

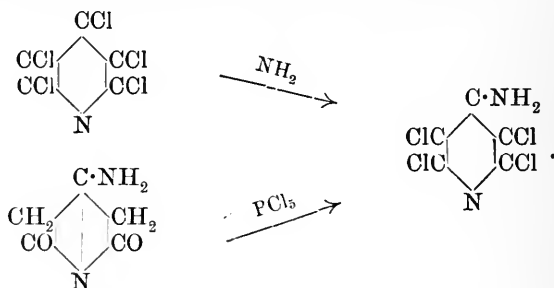
Glutazine was originally prepared by Stokes and von Pechmann (*Ber.*, 1886, 19, 2696) by acting on ethyl amino- $\beta$ -hydroxyglutamate,  $\text{CONH}_2 \cdot \text{CH}_2 \cdot \text{C}(\text{OH})(\text{NH}_2) \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$ , obtained from ethyl acetonedicarboxylate and ammonia, with alkaline carbonates. They considered that its constitution must be represented by one of the two following formulæ :



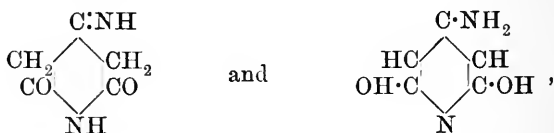
but thought formula II the more probable owing to the analogy between the action of ammonia on ethyl acetonedicarboxylate and its action on ethyl acetoacetate which, as Collie (*Annalen*, 1884, 226, 298) had shown, forms first an aminohydroxy-compound which by loss of water passes into ethyl aminocrotonate,

$\text{MeC}(\text{OH})(\text{NH}_2) \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et} \longrightarrow \text{MeC}(\text{NH}_2) \cdot \text{CH} \cdot \text{CO}_2\text{Et} + \text{H}_2\text{O}$ ; later, von Pechmann (*Ber.*, 1887, 20, 2655), as a result of the study of the action of nitrous acid on glutazine definitely decided in favour of formula I. In spite of this opinion, Sell and Dootson (*Trans.*, 1898, 73, 777) considered that formula II best represented the constitution of glutazine and based their conclusion on the identity of a tetra-chloroaminopyridine, prepared by the action of ammonia on penta-

chloropyridine, with a substance obtained by Stokes and von Pechmann by the interaction of phosphorus pentachloride and glutazine :



From the methods of synthesis described by us, there can be no doubt that glutazine possesses a constitution represented by formula I. The production of the tetrachloroaminopyridine described by Sell and Dootson can be readily understood if the probability of glutazine reacting in the two forms :



is taken into consideration.

The view that glutazine is capable of reacting in both forms receives support not only from the acid and basic character of the many derivatives of glutazine that we have investigated, but also from the close analogy between this substance and 2:4:6-trioxypyridine, which, as Stokes and von Pechmann showed, reacts both as a phenol and a base.

The chief fact which led von Pechmann to the conclusion that the imino-group was present in glutazine was the formation of nitroso-nitroglutazine by the action of nitrous acid. His method consisted in dissolving glutazine in alkali, adding the requisite quantity of sodium nitrite solution, and then pouring the mixture into dilute acetic acid. A sodium salt,  $\text{NaC}_5\text{H}_3\text{O}_5\text{N}_4 \cdot 2\text{H}_2\text{O}$ , slowly separated, which gave the Liebermann reaction, and on warming with dilute sulphuric acid gave off nitrous acid. We have repeated this reaction by applying it to the glutazine prepared by us, with results which confirm von Pechmann's conclusions.

Glutazine also, as von Pechmann showed, is very quickly hydrolysed to the corresponding trioxypyridine on boiling with concentrated hydrochloric acid.

It is remarkable that all the substituted derivatives of glutazine

described by us react quite differently from glutazine itself. They may be divided into three classes :

1. The mono-substitution derivatives :

Ethyl glutazinecarboxylate,  $\text{NH} \begin{smallmatrix} \text{CO} \text{---} \text{CH}_2 \\ \text{CO} \cdot \text{CH}(\text{CO}_2\text{Et}) \end{smallmatrix} \text{C:NH}$ , methylglutazine,  $\text{NH} \begin{smallmatrix} \text{CO} \cdot \text{CHMe} \\ \text{CO} \text{---} \text{CH}_2 \end{smallmatrix} \text{C:NH}$ , ethylglutazine,  $\text{NH} \begin{smallmatrix} \text{CO} \cdot \text{CHEt} \\ \text{CO} \text{---} \text{CH}_2 \end{smallmatrix} \text{C:NH}$ , and glutazine cyanide,  $\text{NH} \begin{smallmatrix} \text{CO} \text{---} \text{CH}_2 \\ \text{CO} \cdot \text{CH}(\text{CN}) \end{smallmatrix} \text{C:NH}$ .

These compounds react with nitrous acid to form oximes of the type  $\text{NH} \begin{smallmatrix} \text{CO} \text{---} \text{CHR} \\ \text{CO} \cdot \text{C}(\text{:NOH}) \end{smallmatrix} \text{C:NH}$ , which are acid substances, forming coloured salts with alkalis, and are characterised by giving, in neutral solution, intense colours with ferrous sulphate. These mono-substitution products of glutazine are unattacked by strong mineral acids even on prolonged boiling.

II. The di-substitution products :

Ethyl methylglutazinecarboxylate,  $\text{NH} \begin{smallmatrix} \text{CO} \text{---} \text{CHMe} \\ \text{CO} \cdot \text{CH}(\text{CO}_2\text{Et}) \end{smallmatrix} \text{C:NH}$ , ethyl ethylglutazinecarboxylate,  $\text{NH} \begin{smallmatrix} \text{CO} \text{---} \text{CHEt} \\ \text{CO} \cdot \text{CH}(\text{CO}_2\text{Et}) \end{smallmatrix} \text{C:NH}$ , and dimethylglutazine,  $\text{NH} \begin{smallmatrix} \text{CO} \cdot \text{CHMe} \\ \text{CO} \cdot \text{CHMe} \end{smallmatrix} \text{C:NH}$ .

These compounds react with nitrous acid to form the corresponding pyridine derivatives with the evolution of free nitrogen. They are not hydrolysed by mineral acids.

III. The tri-substitution products :

Ethyl dimethylglutazinecarboxylate,  $\text{NH} \begin{smallmatrix} \text{CO} \text{---} \text{CHMe} \\ \text{CO} \cdot \text{CMe}(\text{CO}_2\text{Et}) \end{smallmatrix} \text{C:NH}$ .

This compound is unacted on by nitrous acid, and on boiling with mineral acids is hydrolysed partially to dimethylglutazine and partially to the corresponding pyridine derivative, whilst on treatment with caustic potash solution the former substance is alone produced.

Incidentally it may be mentioned that ethyl  $\beta$ -imino- $\alpha$ -cyano- $\alpha\alpha'$ -trimethylglutarate,  $\text{CO}_2\text{Et} \cdot \text{CMe}_2 \cdot \text{C}(\text{:NH}) \cdot \text{CMe}(\text{CN}) \cdot \text{CO}_2\text{Et}$ , shows no tendency to pass into a ring compound, but on treatment with concentrated sulphuric acid is hydrolysed to straight chain degradation products.

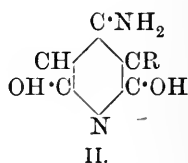
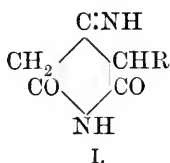
There seems to have been no work done on the nature of the interaction of the group  $\text{C:NH}$  with nitrous acid. And although von Pechmann concluded that this group was present in glutazine from the fact that on treatment with nitrous acid it yielded a nitrosoamine, yet from an examination of the many substances prepared by us, and

which undoubtedly contain this group, not one has been found to react in this way.

We have still under investigation a number of compounds containing this group which have been prepared by the interaction of ethyl sodiocyanoacetate with ethyl malonate, ethyl acetonedicarboxylate, and ethyl acetoacetate, and hope by their help to obtain some further insight into this question.

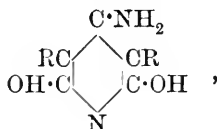
Meanwhile, from the experimental evidence at hand, it is possible to surmise the probable nature of the difference between glutazine and its di- and tri-substitution derivatives.

In the first place, it is evident that the mono-substitution products react in the two forms :

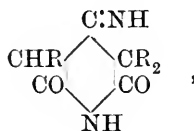


The behaviour towards nitrous acid is best accounted for by formula I, whereas the stability of the compounds towards acid hydrolysing agents is best explained by formula II.

In the second place, it is certain that di-substitution products react only in the form



since this alone explains the formation of the pyridine derivative with nitrous acid and the stability of the compound towards acid hydrolysing agents. In the third place, it follows that the tri-substitution derivatives react only in the form

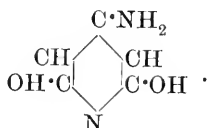
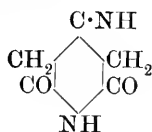


since they are unacted on by nitrous acid and are readily hydrolysed to the corresponding pyridine on treatment with acid hydrolysing agents.

With regard to the constitution of glutazine itself, it is difficult to suggest any formula which adequately explains its reactions.

The formation of the nitrosoamine with nitrous acid would indicate

the grouping  $\begin{smallmatrix} \text{C} \\ \diagup \quad \diagdown \\ \text{C} \end{smallmatrix} > \text{NH}$ , whereas the formation of trioxypyridine by the action of acids, and the formation of tetrachloroaminopyridine by the action of phosphorus pentachloride would seem to show that it can react in the forms

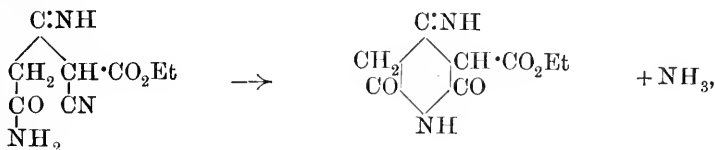


We hope, as the result of the future study of similarly constituted compounds, to arrive at some definite conclusion as to the nature of this substance.

As already mentioned, Stokes and von Pechmann prepared glutazine by the action of alkali carbonates on ethyl amino- $\beta$ -hydroxyglutamate,  $\text{CONH}_2 \cdot \text{CH}_2 \cdot \text{C}(\text{OH})(\text{NH}_2) \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$ .

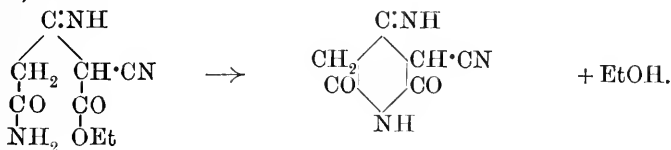
A similar compound, namely, ethyl  $\beta$ -imino- $\alpha$ -cyanoglutamate,  $\text{CONH}_2 \cdot \text{CH}_2 \cdot \text{C}(\text{NH}) \cdot \text{CH}(\text{CN}) \cdot \text{CO}_2\text{Et}$ , can be prepared by the action of alcoholic ammonia on ethyl  $\beta$ -imino- $\alpha$ -cyanoglutarate. From this substance, a glutazine derivative can be prepared in two ways.

1. By the action of concentrated sulphuric acid forming ethyl glutazinecarboxylate,



and

2. By the action of sodium carbonate solution forming glutazine cyanide,



Both these compounds yield glutazine on hydrolysis with caustic potash.

## EXPERIMENTAL.

*Preparation of Ethyl  $\beta$ -Imino- $\alpha$ -cyanoglutarate,*  
 $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{C}(\text{:NH})\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}.$ 

In order to prepare this substance, 11.5 grams of sodium were dissolved in 122 grams of alcohol, and the solution, after being mixed with 113 grams of ethyl cyanoacetate, was heated on the water-bath for 2 hours. The white sodium compound of ethyl cyanoacetate which is in the first instance precipitated, rapidly passes into solution, and after heating for the requisite time the contents of the flask will be observed to consist of a viscid, brown liquid, which sets to a jelly-like mass on cooling. On adding water, this jelly forms a clear solution, showing a slightly alkaline reaction; after some time, an oil begins to separate and the solution then becomes markedly alkaline.

The separation of this oil, which is due to the gradual decomposition of the sodium compound of ethyl  $\beta$ -imino- $\alpha$ -cyanoglutarate by the action of the water, can be hastened by rendering the solution strongly acid by means of hydrochloric acid. The acidified solution was then extracted with ether, the ethereal extract washed successively with water and dilute aqueous sodium carbonate, dried, and distilled until free from ether. The residue consisted of a viscid syrup, which gradually solidified to a hard, crystalline cake, the yield being about 80 per cent. of the theory.

When recrystallised from dilute alcohol, ethyl  $\beta$ -imino- $\alpha$ -cyanoglutarate is obtained in well-defined needles melting at  $53^\circ$ .

0.2057 gave 0.4168  $\text{CO}_2$  and 0.1066  $\text{H}_2\text{O}$ .  $\text{C} = 55.26$ ;  $\text{H} = 5.76$ .

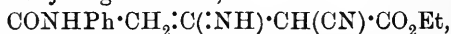
0.2165 „ 0.4390  $\text{CO}_2$  „ 0.1130  $\text{H}_2\text{O}$ .  $\text{C} = 55.3$ ;  $\text{H} = 5.8$ .

0.2064 „ 19.6 c.c. nitrogen at  $15^\circ$  and 780 mm.  $\text{N} = 11.6$ .

$\text{C}_{10}\text{H}_{14}\text{O}_4\text{N}_2$  requires  $\text{C} = 55.4$ ;  $\text{H} = 5.9$ ;  $\text{N} = 11.8$  per cent.

Ethyl  $\beta$ -imino- $\alpha$ -cyanoglutarate undergoes rapid decomposition when distilled in large quantities under diminished pressure, but when a small quantity is rapidly distilled, the pure substance passes over at  $237^\circ/25$  mm.; it is easily soluble in most of the usual organic solvents excepting light petroleum, and instantly dissolves in a cold, strong aqueous sodium hydroxide without undergoing hydrolysis, since on acidifying the ethereal salt is recovered unchanged. In alcoholic solution, it gives no coloration with ferric chloride.

Ethyl  $\beta$ -imino- $\alpha$ -cyanoglutanilide,



is prepared by boiling ethyl  $\beta$ -imino- $\alpha$ -cyanoglutarate with excess of aniline and pouring the product into dilute hydrochloric acid; it

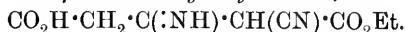
crystallises from absolute alcohol in fine, lustrous plates melting at  $180^{\circ}$ .

0.2047 gave 0.4625  $\text{CO}_2$  and 0.1076  $\text{H}_2\text{O}$ .  $\text{C} = 61.62$ ;  $\text{H} = 5.7$ .

$\text{C}_{14}\text{H}_{15}\text{O}_3\text{N}_3$  requires  $\text{C} = 61.54$ ;  $\text{H} = 5.5$  per cent.

*Action of Hydrolytic Agents on Ethyl  $\beta$ -Imino- $\alpha$ -cyanoglutarate.*

I. *Action of Sodium Carbonate Solution. Formation of Ethyl Hydrogen  $\beta$ -Imino- $\alpha$ -cyanoglutarate,*



Ethyl  $\beta$ -imino- $\alpha$ -cyanoglutarate rapidly dissolves when boiled with a dilute solution of sodium carbonate, and if, when it has completely dissolved, the solution is acidified, a copious precipitate of the ethyl hydrogen ester is formed. This compound crystallises from hot water, in which it is readily soluble, in the form of large, transparent prisms, which, when dry, melt at  $140^{\circ}$ , giving off carbon dioxide at about  $160^{\circ}$ , and between these temperatures being slowly transformed into ethyl glutazinecarboxylate.

0.2534 gave 0.4497  $\text{CO}_2$  and 0.1190  $\text{H}_2\text{O}$ .  $\text{C} = 48.4$ ;  $\text{H} = 5.22$ .

0.2378 ,, 28.3 c.c. nitrogen at  $16^{\circ}$  and 770 mm.  $\text{N} = 13.9$ .

$\text{C}_8\text{H}_{10}\text{O}_4\text{N}_2$  requires  $\text{C} = 48.5$ ;  $\text{H} = 5.00$ ;  $\text{N} = 14.1$  per cent.

This ethyl hydrogen salt appears to crystallise with 1 mol. of water of crystallisation, but as no definite results could be obtained on analysis the above figures refer to the substance dried at  $100^{\circ}$ .

The silver salt is formed as a white, gelatinous precipitate, when the calculated quantity of a silver nitrate solution is added to a solution of the ammonium salt of the acid which should be produced by neutralising a solution of the acid with ammonia in the cold.

0.2671 gave 0.1399 Ag.  $\text{Ag} = 52.4$ .

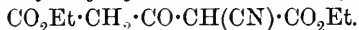
$\text{C}_8\text{H}_9\text{O}_4\text{N}_2\text{Ag}$  requires  $\text{Ag} = 52.6$  per cent.

*Esterification of Ethyl Hydrogen  $\beta$ -Imino- $\alpha$ -cyanoglutarate.*—Ethyl hydrogen  $\beta$ -imino- $\alpha$ -cyanoglutarate (25 grams) was dissolved in 70 grams of absolute alcohol and 25 grams of concentrated sulphuric acid added, the whole being left for 12 hours. On adding water, a quantity of oil separated, the ethereal extract of which, when washed with aqueous sodium carbonate and distilled, yielded a product boiling at  $197^{\circ}$  under ordinary pressure, and giving on analysis numbers corresponding with ethyl malonate.

0.596 gave 0.5027  $\text{CO}_2$  and 0.1831  $\text{H}_2\text{O}$ .  $\text{C} = 52.8$ ;  $\text{H} = 7.4$ .

$\text{C}_7\text{H}_{12}\text{O}_4$  requires  $\text{C} = 52.5$ ;  $\text{H} = 7.5$  per cent.

The sodium carbonate washings of the above extract gave an oil on acidifying which slowly became solid, and was crystallised from dilute alcohol, from which solvent it separated in large prisms which melted at 43°. It is probably *ethyl cyanoacetonedicarboxylate*,



0.2148 gave 0.4173  $\text{CO}_2$  and 0.1166  $\text{H}_2\text{O}$ .  $\text{C} = 52.98$ ;  $\text{H} = 6.03$ .

$\text{C}_{10}\text{H}_{13}\text{O}_5\text{N}$  requires  $\text{C} = 52.9$ ;  $\text{H} = 5.7$  per cent.

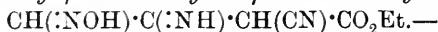
This substance is soluble in sodium carbonate solution and gives a deep red coloration with ferric chloride.

On adding alkali to the mother liquors of the foregoing esterification until the solution is only slightly acid, a copious precipitate of ethyl glutazinecarboxylate is produced.

The following quantities were obtained in the foregoing experiment from 25 grams of ethyl hydrogen  $\beta$ -imino- $\alpha$ -cyanoglutarate.

Ethyl malonate, 10 grams; ethyl cyanoacetonedicarboxylate, 1 gram; and ethyl glutazinecarboxylate, 12 grams.

*Formation of Ethyl  $\beta$ -Imino- $\alpha$ -cyano- $\gamma$ -isonitrosobutyrate,*



This oxime is best prepared by dissolving the ethyl hydrogen salt in sodium hydroxide solution, and after mixing with this the requisite quantity of aqueous sodium nitrite, the mixture is poured into a 50 per cent. solution of acetic acid. After a short time, a crystalline substance is deposited which separates from absolute alcohol in well-defined prisms melting at 156° and instantly charring.

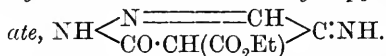
0.1652 gave 0.2804  $\text{CO}_2$  and 0.0744  $\text{H}_2\text{O}$ .  $\text{C} = 46.29$ ;  $\text{H} = 5.00$ .

0.1701 „ 34.1 c.c. nitrogen at 14.5° and 749 mm.  $\text{N} = 23.6$ .

$\text{C}_7\text{H}_9\text{O}_3\text{N}_3$  requires  $\text{C} = 45.9$ ;  $\text{H} = 4.9$ ;  $\text{N} = 22.09$  per cent.

The oxime dissolves in aqueous sodium carbonate forming a yellow solution.

*Formation of Ethyl 4-Imino-6-keto-1:5-dihydropyridazine-5-carboxyl-*



When the oxime is heated with concentrated sulphuric acid, considerable heat is generated and usually the whole mass chars, but if the solid is added in small quantities to the concentrated acid and the mixture is kept well cooled, the compound rapidly dissolves, forming a clear solution, which, when diluted with water and rendered alkaline with aqueous sodium carbonate, deposits a large quantity of an amorphous basic substance.

An analysis of the air-dried product showed it to have the formula of an ammonium base,  $\text{C}_7\text{H}_{10}\text{O}_3\text{N}_3 \cdot \text{OH}$ .

0.2133 gave 0.3248  $\text{CO}_2$  and 0.1098  $\text{H}_2\text{O}$ .  $\text{C} = 41.53$ ;  $\text{H} = 5.46$ .

$\text{C}_7\text{H}_{11}\text{O}_4\text{N}_3$  requires  $\text{C} = 41.8$ ;  $\text{H} = 5.5$  per cent.

When dried in a vacuum desiccator for 5 days, the substance gave numbers corresponding with the free base.

0.2517 gave 0.4217  $\text{CO}_2$  and 0.1088  $\text{H}_2\text{O}$ .  $\text{C} = 45.69$ ;  $\text{H} = 4.8$  per cent.

0.2153 gave 41.6 c.c. nitrogen at  $15^\circ$  and 763 mm.  $\text{N} = 23.1$ .

$\text{C}_7\text{H}_9\text{O}_3\text{N}_3$  requires  $\text{C} = 45.9$ ;  $\text{H} = 4.9$ ;  $\text{N} = 22.9$  per cent.

Neither the anhydrous nor the hydrated base has any definite melting point, but both forms deflagrate at about  $170^\circ$ . On mixing with water, the anhydrous base becomes very hot and passes into its hydrated form.

The *hydrochloride*,  $\text{C}_7\text{H}_9\text{O}_3\text{N}_3\cdot\text{HCl}$ , was made by dissolving the base in dilute hydrochloric acid, filtering, and evaporating nearly to dryness; the solid which separated was then spread on a porous plate and dried in a desiccator over potassium hydroxide. It was analysed by weighing a quantity into a beaker, dissolving in water, and adding silver nitrate solution acidified with nitric acid.

0.2210 gave 0.1421  $\text{AgCl}$ .  $\text{Cl} = 15.9$ .

$\text{C}_7\text{H}_{10}\text{O}_3\text{N}_3\text{Cl}$  requires  $\text{Cl} = 16.1$  per cent.

The base undergoes a curious decomposition when boiled with a strong aqueous solution of sodium hydroxide, eliminating two of its nitrogen atoms in the form of free nitrogen. The products which are formed under these circumstances are still under investigation. The *hydrazone*, prepared by dissolving the base in dilute acetic acid, adding a solution of phenylhydrazine acetate, and boiling for a short time, is precipitated on cooling as an oil which slowly solidifies, and separates from hot absolute alcohol in the form of small, yellow needles melting at  $173^\circ$ .

0.1714 gave 0.3389  $\text{CO}_2$  and 0.0931  $\text{H}_2\text{O}$ .  $\text{C} = 53.92$ ;  $\text{H} = 6.03$ .

$\text{C}_{13}\text{H}_{17}\text{O}_5\text{N}_3$  requires  $\text{C} = 53.6$ ;  $\text{H} = 5.8$  per cent.

*Ethyl  $\beta$ -imino- $\alpha$ -cyanobutyrate*,  $\text{MeC}(\text{:NH})\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}$ , is formed in small quantities when ethyl hydrogen  $\beta$ -imino- $\alpha$ -cyanoglutarate is rapidly distilled; it is, however, produced quantitatively when the ammonium salt of this acid is distilled under diminished pressure. It crystallises from absolute alcohol in large, transparent prisms, which melt at  $181^\circ$  and boil at  $210^\circ/30$  mm.

0.2030 gave 0.4050  $\text{CO}_2$  and 0.1210  $\text{H}_2\text{O}$ .  $\text{C} = 54.38$ ;  $\text{H} = 6.6$ .

0.2157 „ 32.3 c.c. nitrogen at  $18^\circ$  and 780 mm.  $\text{N} = 18.4$ .

$\text{C}_7\text{H}_{10}\text{O}_2\text{N}_2$  requires  $\text{C} = 54.5$ ;  $\text{H} = 6.5$ ;  $\text{N} = 18.2$  per cent.

Ethyl  $\beta$ -imino- $\alpha$ -cyanobutyrate is slowly formed when either the sodium or ammonium salt of ethyl hydrogen  $\beta$ -imino- $\alpha$ -cyanoglutarate is boiled with water.

*Ethyl cyanoacetoacetate*,  $\text{MeCO}\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}$ , is formed by the hydrolysis of ethyl  $\beta$ -imino- $\alpha$ -cyanobutyrate with dilute sulphuric acid. In order that the hydrolysis may not proceed too far, it is necessary to remove the first product as soon as it is formed. This can be readily done by passing a current of steam through the flask containing the hydrolysing mixture, which causes the ethyl cyanoacetoacetate to pass over into a receiver and prevents it from being further hydrolysed by the action of the sulphuric acid. Ethyl cyanoacetoacetate prepared in this way melts at  $26^\circ$  and boils at  $119^\circ/20\text{ mm.}$ , it is in all respects identical with the substance prepared by Haller and Held.

0.2833 gave 0.5573  $\text{CO}_2$  and 0.1525  $\text{H}_2\text{O}$ .  $\text{C}=53.65$ ;  $\text{H}=5.98$ .

$\text{C}_7\text{H}_9\text{O}_3\text{N}$  requires  $\text{C}=54.2$ ;  $\text{H}=5.8$  per cent.

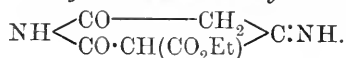
## II. Action of Sodium Hydroxide Solution. Formation of Malonic Acid.

As already mentioned, ethyl  $\beta$ -imino- $\alpha$ -cyanoglutarate is dissolved by cold aqueous sodium hydroxide without undergoing hydrolysis. If, however, the solution is boiled, rapid hydrolysis ensues, and if the boiling is continued until the evolution of ammonia has ceased, the product on acidifying and extracting will be found to yield only malonic acid melting at  $132^\circ$ .

A decomposition of the same nature is undergone by ethyl hydrogen  $\beta$ -imino- $\alpha$ -cyanoglutarate and ethyl  $\beta$ -imino- $\alpha$ -cyanobutyrate, the former yielding, on prolonged boiling with sodium hydroxide solution, malonic acid, and the latter a mixture of malonic and acetic acids.

## III. Action of Concentrated Sulphuric Acid. Formation of Pyridine Derivatives.

*Ethyl Glutazinecarboxylate.*



When ethyl  $\beta$ -imino- $\alpha$ -cyanoglutarate is dissolved in cold concentrated sulphuric acid and the solution left for 3 hours, a copious precipitate of this substance is produced on the addition of water. It crystallises from glacial acetic acid in lustrous plates, sometimes possessing a faint green tinge, and does not appear to melt when heated.

0.2590 gave 0.4603 CO<sub>2</sub> and 0.1260 H<sub>2</sub>O. C = 48.47; H = 5.41.

0.2336 „ 28.4 c.c. nitrogen at 13.5° and 754 mm. N = 14.5.

C<sub>8</sub>H<sub>10</sub>O<sub>4</sub>N<sub>2</sub> requires C = 48.5; H = 5.1; N = 14.1 per cent.

This substance is sparingly soluble in hot water, and its solution gives a deep red colour with ferric chloride. It forms salts with both acids and alkalis, but the former are unstable in solution.

The *hydrochloride*, C<sub>8</sub>H<sub>10</sub>O<sub>4</sub>N<sub>2</sub>.HCl, crystallises from concentrated hydrochloric acid in small prisms.

0.2357 gave 0.1423 AgCl. HCl = 15.4.

C<sub>8</sub>H<sub>10</sub>O<sub>4</sub>N<sub>2</sub>.HCl requires 15.56 per cent.

It is readily soluble in water, but is almost immediately decomposed with formation of the insoluble base.

The *oxime*, HN<CO---C(:NOH)>C:NH, is best prepared by dissolving ethyl glutazinecarboxylate in caustic soda solution containing the requisite quantity of sodium nitrite, and pouring the mixture into dilute acetic acid; a precipitate is immediately formed which can be recrystallised from dilute acetic acid, from which solvent it separates in the form of fine yellow needles.

0.1640 gave 0.2557 CO<sub>2</sub> and 0.0648 H<sub>2</sub>O. C = 42.47; H = 4.38.

0.1746 „ 30.7 c.c. nitrogen at 14.5° and 748 mm. N = 18.7.

C<sub>8</sub>H<sub>9</sub>O<sub>5</sub>N<sub>3</sub> requires C = 42.3; H = 4.0; N = 18.5 per cent.

This substance is an acid and dissolves in aqueous sodium carbonate to form a deep red solution, which, on concentrating, deposits the sodium salt in the form of a brick-red powder. A neutral solution of either the ammonium or sodium salt gives a characteristic deep blue coloration with ferrous sulphate, which on boiling is converted into a deep indigo-blue precipitate. The free acid dissolves in concentrated sulphuric acid and is precipitated unchanged on adding water. After prolonged boiling with dilute sulphuric acid, it passes into solution and on cooling straw-coloured needles are deposited. These are still under investigation.

The *dibenzoyl* derivative, PhCO·N<CO---CH<sub>2</sub>>C:N·COPh, can be prepared by boiling ethyl glutazinecarboxylate with excess of benzoyl chloride in a Geissler flask for 3 hours.

On cooling, a crystalline precipitate slowly separates, which can be recrystallised from hot glacial acetic acid and obtained in small needles melting at 220°.

0.2230 gave 0.5290 CO<sub>2</sub> and 0.0863 H<sub>2</sub>O. C = 64.70; H = 4.3.

C<sub>22</sub>H<sub>18</sub>O<sub>6</sub>N<sub>2</sub> requires C = 65.0; H = 4.4 per cent.

*Preparation of Glutazine from Ethyl Glutazinecarboxylate.*

Glutazine can be prepared from the ethyl salt of its carboxylic acid by hydrolysis with caustic soda solution. The stability of the ethyl salt, however, is such that it is necessary almost to fuse it with caustic soda before hydrolysis ensues.

It was found most convenient to dissolve about one gram of the ethyl salt in potassium hydroxide solution contained in a wide-mouthed tube, and boil over the free flame until the odour of ammonia became perceptible at the mouth of the tube. On acidifying with acetic acid, a crystalline substance separated on cooling; this was recrystallised from water, from which solvent it separated in the form of rectangular plates.

0.2207 gave 0.3867  $\text{CO}_2$  and 0.1031  $\text{H}_2\text{O}$ .  $\text{C} = 47.78$ ;  $\text{H} = 5.19$ .

$\text{C}_5\text{H}_6\text{O}_2\text{N}_2$  requires  $\text{C} = 47.6$ ;  $\text{H} = 4.8$  per cent.

Glutazine obtained in this way is identical with the compound prepared by Stokes and Pechmann; it melts with decomposition at about  $300^\circ$  and gives in aqueous solution a red coloration with ferric chloride, which changes to green on boiling. The dibenzoyl derivative melts at  $215\text{--}216^\circ$ .

2:4:6-Trioxypyridine, produced from glutazine by the action of concentrated hydrochloric acid, as described by Stokes and Pechmann, is a heavy, yellow, sandy powder which decomposes at about  $220^\circ$ , without melting, and gives with ferric chloride in aqueous solution a deep red coloration.

0.2236 gave 0.3868  $\text{CO}_2$  and 0.0745  $\text{H}_2\text{O}$ .  $\text{C} = 47.18$ ;  $\text{H} = 3.72$ .

$\text{C}_5\text{H}_5\text{O}_3\text{N}$  requires  $\text{C} = 47.24$ ;  $\text{H} = 3.94$  per cent.

IV. *Action of Dilute Sulphuric Acid. Formation of the Sulphate of 2:4:6-Trioxypyridine Anhydride,  $\text{C}_{10}\text{H}_8\text{O}_5\text{N}_2, \text{H}_2\text{SO}_4, 3\text{H}_2\text{O}$ .*

When ethyl  $\beta$ -imino- $\alpha$ -cyanoglutarate is boiled with a solution containing 1 part of sulphuric acid to three parts of water, it gradually dissolves, and if, after heating for three hours, the solution is cooled, well defined crystals of the above sulphate separate. It is a fairly stable substance and can be recrystallised from water, separating in the form of lustrous plates which melt at  $115^\circ$ ; it is, however, decomposed on prolonged boiling.

0.4836 gave 0.3113  $\text{BaSO}_4$ .  $\text{S} = 8.84$ .

0.2140 ,, 12.55 c.c. of nitrogen at  $15.5^\circ$  and 742 mm.  $\text{N} = 6.82$ .

0.1995 ,, 0.2302  $\text{CO}_2$  and 0.0790  $\text{H}_2\text{O}$ .  $\text{C} = 31.42$ ;  $\text{H} = 4.4$ .

$\text{C}_{10}\text{H}_8\text{O}_5\text{N}_2, \text{H}_2\text{SO}_4, 3\text{H}_2\text{O}$  requires  $\text{C} = 31.74$ ;  $\text{H} = 4.2$ ;  $\text{S} = 8.46$ ;  $\text{N} = 7.4$  per cent.

The three molecules of water are expelled if the hydrated sulphate is heated at  $100^{\circ}$  for 4 or 5 hours.

0.2102 gave 0.1441  $\text{BaSO}_4$ .  $S = 9.42$ .

$\text{C}_{10}\text{H}_8\text{O}_5\text{N}_2 \cdot \text{H}_2\text{SO}_4$  requires  $S = 9.5$  per cent.

The same substance is produced in the form of fine needles when the hydrated sulphate is recrystallised from concentrated sulphuric acid; it however, readily takes up water from the air and passes into the hydrated condition.

If the aqueous solution of the sulphate is made alkaline with ammonia and then acidified with acetic acid, the *acid ammonium* salt is precipitated as a yellow powder.

0.1427 gave 0.2486  $\text{CO}_2$  and 0.0581  $\text{H}_2\text{O}$ .  $C = 47.51$ ;  $H = 4.53$ .

$\text{C}_{10}\text{H}_8\text{O}_5\text{N}_2 \cdot \text{NH}_3$  requires  $C = 47.4$ ;  $H = 4.3$  per cent.

2:4:6-Trioxypyridine Anhydride,  $\text{C}_{10}\text{H}_8\text{O}_5\text{N}_2$ .—As Stokes and von Pechmann showed, trioxypyridine anhydride is a dibasic acid. The free acid was therefore prepared from the sulphate in the following way. A weighed quantity of the hydrated sulphate was dissolved in cold water, neutralised with ammonia, and an equivalent quantity of hydrated sulphate dissolved in cold water was added to it. On mixing the two solutions, trioxypyridine anhydride was at once precipitated as a yellow solid.

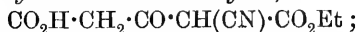
0.1972 gave 0.3673  $\text{CO}_2$  and 0.0639  $\text{H}_2\text{O}$ .  $C = 50.61$ ;  $H = 3.62$ .

$\text{C}_{10}\text{H}_8\text{O}_5\text{N}_2$  requires  $C = 50.8$ ;  $H = 3.4$  per cent.

Trioxypyridine anhydride is converted into trioxypyridine by evaporating its aqueous solution and extracting the residue with alcohol.

#### V. Action of Hydrochloric Acid. Formation of 2:4:6-Trioxypyridine.

Ethyl  $\beta$ -imino- $\alpha$ -cyanoglutarate, when boiled with concentrated hydrochloric acid, rapidly passes into solution, and if, when all has dissolved, the solution is cooled, it deposits a considerable quantity of a crystalline substance: this was found to consist of a mixture of two compounds which could be separated by recrystallisation from water. The more insoluble proved to be ethyl hydrogen  $\beta$ -imino- $\alpha$ -cyanoglutarate,  $\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{C}(\text{NH}) \cdot \text{CH}(\text{CN}) \cdot \text{CO}_2\text{Et}$ , and the more soluble to be *ethyl hydrogen  $\alpha$ -cyanoacetonedicarboxylate*,



the latter crystallises from water in long, colourless needles which melt at  $145^{\circ}$  and at  $170^{\circ}$  give off carbon dioxide, being converted between these temperatures into ethyl 2:4:6-trioxypyridine-3-carboxylate.

0.2135 gave 0.3755  $\text{CO}_2$  and 0.0830  $\text{H}_2\text{O}$ .  $\text{C} = 47.97$ ;  $\text{H} = 4.32$ .

$\text{C}_8\text{H}_9\text{O}_5\text{N}$  requires  $\text{C} = 48.2$ ;  $\text{H} = 4.5$  per cent.

The dicarboxylate gives a red coloration in aqueous solution with ferric chloride.

On addition of water, ethyl glutazinecarboxylate is precipitated from the mother liquors. If, however, the hydrochloric acid solution is heated for five to six hours on the sand-bath, and the resulting solution evaporated to dryness on the water-bath, a residue is obtained which consists of a hydrochloride. After a rough estimation of the quantity of hydrochloric acid had been made, the calculated quantity of sodium carbonate solution was added to neutralise the hydrochloric acid present, when a white precipitate was at once formed which, on collecting, proved to be 2 : 4 : 6-trioxypyridine.

0.2154 gave 0.3712  $\text{CO}_2$  and 0.0756  $\text{H}_2\text{O}$ .  $\text{C} = 47.01$ ;  $\text{H} = 3.9$ .

$\text{C}_5\text{H}_5\text{O}_3\text{N}$  requires  $\text{C} = 47.2$ ;  $\text{H} = 3.9$  per cent.

When fused with ammonium acetate for from two to three minutes and then extracted with hot alcohol, the alcoholic solution on evaporation yielded a residue which crystallised from water in small plates, and gave in aqueous solution a deep red coloration with ferric chloride, changing to green on boiling. The substance was evidently therefore glutazine.

*Action of Ammonia. Formation of Ethyl  $\beta$ -Imino- $\alpha$ -cyanoglutarate,*  
 $\text{CONH}_2 \cdot \text{CH}_2 \cdot \text{C}(\text{:NH}) \cdot \text{CH}(\text{CN}) \cdot \text{CO}_2\text{Et}$ .

Ethyl  $\beta$ -imino- $\alpha$ -cyanoglutarate dissolves when warmed with concentrated ammonia solution, and on cooling the above substance separates out in the form of a white, crystalline powder. It is best prepared, however, by dissolving the ethyl salt in alcohol and saturating the solution with ammonia gas, or by dissolving it in alcohol (3 vols.) and adding 1 vol. of 0.880 ammonia solution. By either method, a practically quantitative yield of the glutamate separates on standing.

It is readily soluble in hot water, sparingly in cold, and separates from its hot aqueous solution in small needles which melt at  $195^\circ$  with decomposition.

0.2431 gave 45.3 c.c nitrogen at  $19^\circ$  and 755 mm.  $\text{N} = 21.8$ .

$\text{C}_8\text{H}_{11}\text{O}_3\text{N}_3$  requires  $\text{N} = 21.3$  per cent.

*Action of Concentrated Sulphuric Acid on the Amide. Formation of Ethyl Glutazinecarboxylate.*—One gram of the pure, finely-ground amide was added gradually to 5 c.c. of concentrated sulphuric acid, the solution being kept cool under the tap. When all had dissolved, water

was added and the heavy, white precipitate which formed collected and recrystallised from glacial acetic acid. An analysis proved it to be ethyl glutazinecarboxylate.

0.1563 gave 0.2796  $\text{CO}_2$  and 0.0769  $\text{H}_2\text{O}$ .  $\text{C} = 48.82$ ;  $\text{H} = 5.47$ .

$\text{C}_8\text{H}_{10}\text{O}_4\text{N}_2$  requires  $\text{C} = 48.5$ ;  $\text{H} = 5.1$  per cent.

*Action of Sodium Carbonate Solution on the Amide. Formation of Glutazine Cyanide*,  $\text{NH} \left\langle \begin{array}{c} \text{CO} - \text{CH}_2 \\ \text{CO} \cdot \text{CH}(\text{CN}) \end{array} \right\rangle \text{C} \cdot \text{NH}$ .—Five grams of the amide were dissolved in sodium carbonate solution and boiled for 1 hour; alcohol and ammonia were eliminated, and the solution on cooling deposited a small quantity of ethyl  $\beta$ -imino- $\alpha$ -cyanobutyrate, melting at  $181^\circ$ . On acidifying the filtered solution with hydrochloric acid, a heavy precipitate of the above cyanide was formed. It can be recrystallised from a large quantity of water, but is more easily obtained pure by dissolving in sodium carbonate solution (in which it dissolves with effervescence) and acidifying hot with acetic acid; on cooling, the pure cyanide separates in the form of colourless needles.

0.2419 gave 0.4249  $\text{CO}_2$  and 0.0802  $\text{H}_2\text{O}$ .  $\text{C} = 47.90$ ;  $\text{H} = 3.68$ .

$\text{C}_6\text{H}_5\text{O}_2\text{N}_3$  requires  $\text{C} = 47.7$ ;  $\text{H} = 3.3$  per cent.

The aqueous solution gives with ferric chloride a reddish-violet coloration changing to brown on boiling. Glutazine cyanide is insoluble in concentrated hydrochloric acid, but dissolves in concentrated sulphuric acid, being reprecipitated on the addition of water; with caustic soda solution, it first forms a sparingly soluble acid salt which dissolves on addition of more alkali.

The *dibenzoyl* derivative is prepared by boiling the cyanide with benzoyl chloride until the evolution of hydrochloric acid ceases; on cooling, a crystalline substance slowly separates, which can be recrystallised from absolute alcohol yielding small plates melting at  $193^\circ$ .

0.2173 gave 0.5317  $\text{CO}_2$  and 0.0688  $\text{H}_2\text{O}$ .  $\text{C} = 66.73$ ;  $\text{H} = 3.52$ .

$\text{C}_{20}\text{H}_{13}\text{O}_4\text{N}_3$  requires  $\text{C} = 66.9$ ;  $\text{H} = 3.6$  per cent.

The *oxime*,  $\text{HN} \left\langle \begin{array}{c} \text{CO} \cdot \text{C}(\text{NOH}) \\ \text{CO} - \text{CH}(\text{CN}) \end{array} \right\rangle \text{C} \cdot \text{NH}$ , is formed by dissolving the cyanide in aqueous caustic soda, adding a solution of the calculated quantity of sodium nitrite, and pouring the mixture into dilute acetic acid. A red solution is formed which quickly deposits red crystals of a sodium salt. These do not give the Liebermann reaction, and on warming with dilute hydrochloric acid yield the free acid having the above formula as a yellow, microcrystalline powder.

The oxime is not decomposed on boiling for a short time with hydro-

chloric acid, and gives with ferrous sulphate in neutral solution a deep indigo-blue coloration.

0.2213 gave 0.3235  $\text{CO}_2$  and 0.0422  $\text{H}_2\text{O}$ .  $\text{C} = 39.87$ ;  $\text{H} = 2.12$ .

$\text{C}_6\text{H}_4\text{O}_3\text{N}_4$  requires  $\text{C} = 40.0$ ;  $\text{H} = 2.2$  per cent.

The substance deflagrates when heated, and does not possess a definite melting point.

*Hydrolysis of the Cyanide. Formation of 2:4:6-Trioxypyridine.*

The cyanide is not readily hydrolysed by hydrochloric acid, and even on prolonged boiling is little changed; it was therefore found advantageous to heat 1 gram with concentrated hydrochloric acid in a sealed tube at  $180^\circ$  for 4 hours. The contents of the tube on evaporating to dryness yielded a residue which, on treatment with sodium carbonate in the manner already described, yielded trioxypyridine, which, on fusion with ammonium acetate, yielded glutazine.

*Conversion of Ethyl Hydrogen  $\beta$ -Imino- $\alpha$ -cyanoglutarate into Ethyl Glutazinecarboxylate.*

In order to show that this molecular change takes place without the presence of water, 5 grams of the finely powdered and carefully purified ethyl hydrogen salt were dried at  $100^\circ$  for 8 hours. The slightly brown substance was then heated to  $145^\circ$  in a tube surrounded by sulphuric acid, and the temperature maintained at this point for 10 minutes.

The solid melted and gradually became yellow, a small quantity of carbon dioxide being eliminated at the same time; it then became solid, and after being heated for the requisite time was extracted with hot absolute alcohol and filtered. The residue weighing 4.2 grams was found to be pure ethyl glutazinecarboxylate, crystallising from glacial acetic acid in characteristic plates.

0.2217 gave 0.3959  $\text{CO}_2$  and 0.1031  $\text{H}_2\text{O}$ .  $\text{C} = 48.7$ ;  $\text{H} = 5.17$ .

$\text{C}_8\text{H}_{10}\text{O}_4\text{N}_2$  requires  $\text{C} = 48.5$ ;  $\text{H} = 5.0$  per cent.

The alcoholic solution on cooling deposited a small quantity of ethyl  $\beta$ -imino- $\alpha$ -cyanobutyrate melting at  $181^\circ$ .

*Conversion of Ethyl Hydrogen Cyanoacetonedicarboxylate into Ethyl*

*2:4:6-Trioxypyridine-3-carboxylate,  $\text{NH} \begin{array}{c} \text{CO} \text{---} \text{CH}_2 \\ \text{CO} \cdot \text{CH}(\text{CO}_2\text{Et}) \end{array} \text{CO}$ .*

The carefully dried ethyl hydrogen salt was heated at  $147^\circ$  for from 10 to 15 minutes. A small quantity of carbon dioxide was eliminated from the melted mass, which subsequently set to a crystal-

line cake. This was purified by rubbing with cold absolute alcohol, filtering, and recrystallising from glacial acetic acid.

Ethyl 2:4:6-trioxypyridine-3-carboxylate is obtained in this way in small plates which melt at a high temperature and give in dilute alcoholic solution a red coloration with ferric chloride. It is soluble in alkalis and in acids.

0.1793 gave 0.3162  $\text{CO}_2$  and 0.0692  $\text{H}_2\text{O}$ .  $\text{C} = 48.10$ ;  $\text{H} = 4.29$ .

$\text{C}_8\text{H}_9\text{O}_5\text{N}$  requires  $\text{C} = 48.2$ ;  $\text{H} = 4.5$  per cent.

2:4:6-Trioxypyridine, prepared from the ethyl salt on hydrolysis with caustic potash, was extracted and purified by the method already given on page 1744, and was identified by conversion into glutazine on fusion with ammonium acetate.

*Action of Methyl Iodide on the Sodium Compound of Ethyl  $\beta$ -Imino- $\alpha$ -cyanoglutarate. Formation of Ethyl  $\beta$ -Imino- $\alpha$ -cyano- $\alpha'$ -methylglutarate,*  
 $\text{CO}_2\text{Et} \cdot \text{CHMe} \cdot \text{C}(\text{:NH}) \cdot \text{CH}(\text{CN}) \cdot \text{CO}_2\text{Et}.$

As already mentioned, after heating molecular proportions of ethyl sodiocyanoacetate and ethyl cyanoacetate in alcoholic solution for 2 hours on the water-bath, a jelly-like mass is obtained: this is the sodium compound,  $\text{CO}_2\text{Et} \cdot \text{CHNa} \cdot \text{C}(\text{:NH}) \cdot \text{CH}(\text{CN}) \cdot \text{CO}_2\text{Et}$ . On adding excess of methyl iodide and boiling, this sodium compound gradually dissolves, and, when all has passed into solution, the above ethyl salt is precipitated on adding water; it distils without decomposition at  $220^\circ/20$  mm. and solidifies on cooling, forming small prisms from dilute alcohol which melt at  $63^\circ$ .

0.2164 gave 0.4356  $\text{CO}_2$  and 0.1287  $\text{H}_2\text{O}$ .  $\text{C} = 54.80$ ;  $\text{H} = 6.61$ .

$\text{C}_{11}\text{H}_{16}\text{O}_4\text{N}_2$  requires  $\text{C} = 55.0$ ;  $\text{H} = 6.7$  per cent.

Ethyl  $\beta$ -imino- $\alpha$ -cyano- $\alpha'$ -methylglutarate is not nearly so readily soluble in sodium carbonate solution as the unmethylated product, and it is necessary to boil the mixture for some time, using a 30 per cent. solution of the alkali, before complete solution is effected. On cooling, a quantity of crystals separated; these, on collecting, proved to be *ethyl  $\alpha$ -cyano- $\beta$ -aminovalerate*,  $\text{EtC}(\text{:NH}) \cdot \text{CH}(\text{CN}) \cdot \text{CO}_2\text{Et}$ , which crystallises from absolute alcohol in small prisms melting at  $121^\circ$ .

0.2071 gave 0.4352  $\text{CO}_2$  and 0.1308  $\text{H}_2\text{O}$ .  $\text{C} = 57.31$ ;  $\text{H} = 7.02$ .

$\text{C}_8\text{H}_{12}\text{O}_2\text{N}_2$  requires  $\text{C} = 57.1$ ;  $\text{H} = 7.1$  per cent.

On acidifying the sodium carbonate mother liquors, a copious precipitate of *ethyl hydrogen  $\beta$ -imino- $\alpha$ -cyano- $\alpha'$ -methylglutarate*,

$\text{CO}_2\text{H} \cdot \text{CHMe} \cdot \text{C}(\text{:NH}) \cdot \text{CH}(\text{CN}) \cdot \text{CO}_2\text{Et},$

separated; this substance crystallises from hot water in glistening

plates, which melt at  $145^{\circ}$ , giving off carbon dioxide at  $160^{\circ}$ , and between these temperatures being gradually transformed into ethyl methylglutazinecarboxylate (see p. 1749).

0.2164 gave 0.4025  $\text{CO}_2$  and 0.1079  $\text{H}_2\text{O}$ .  $\text{C} = 50.73$ ;  $\text{H} = 5.54$ .

$\text{C}_9\text{H}_{12}\text{O}_4\text{N}_2$  requires  $\text{C} = 50.9$ ;  $\text{H} = 5.7$  per cent.

The *silver* salt separates as a white, gelatinous precipitate when a neutral solution of the ammonium salt is mixed with a solution containing the calculated quantity of silver nitrate.

0.2153 gave 0.0724 Ag.  $\text{Ag} = 33.62$ .

$\text{C}_9\text{H}_{11}\text{O}_4\text{N}_2\text{Ag}$  requires  $\text{Ag} = 33.77$  per cent.

The ammonium salt, prepared by evaporating to dryness a solution of the hydrogen salt neutralised with ammonia, is quantitatively converted into ethyl  $\beta$ -imino- $\alpha$ -cyanovalerate on distillation under diminished pressure.

*Ethyl cyanopropionylacetate*,  $\text{EtCO}\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}$ , is prepared by hydrolysing ethyl  $\beta$ -imino- $\alpha$ -cyanovalerate with dilute sulphuric acid, passing at the same time a current of steam through the hydrolysing mixture. The steam carries with it the new ethyl salt, which can be extracted from the steam distillate by means of ether. It is a clear, mobile liquid boiling at  $220$ — $225^{\circ}$  under the ordinary pressure.

0.2645 gave 0.5504  $\text{CO}_2$  and 0.1634  $\text{H}_2\text{O}$ .  $\text{C} = 56.75$ ;  $\text{H} = 6.86$ .

$\text{C}_8\text{H}_{11}\text{O}_3\text{N}$  requires  $\text{C} = 56.8$ ;  $\text{H} = 6.5$  per cent.

Ethyl  $\beta$ -imino- $\alpha$ -cyano- $\alpha'$ -methylglutarate dissolved slowly in aqueous caustic soda, and, on boiling, ammonia and alcohol were evolved. When the odour of ammonia ceased to be apparent, the product was acidified, saturated with ammonium sulphate, and extracted.

The extract was found to consist of methylmalonic acid melting at  $130^{\circ}$ .

0.2321 gave 0.3675  $\text{CO}_2$  and 0.1069  $\text{H}_2\text{O}$ .  $\text{C} = 43.18$ ;  $\text{H} = 5.12$ .

$\text{C}_4\text{H}_6\text{O}_4$  requires  $\text{C} = 43.6$ ;  $\text{H} = 5.4$  per cent.

The extracted mother liquors were evaporated to dryness and extracted with ether in a Soxhlet apparatus; the extract in this case was malonic acid melting at  $132^{\circ}$ .

Ethyl hydrogen  $\beta$  imino- $\alpha$ -cyano- $\alpha'$ -methylglutarate is hydrolysed in the same way with caustic soda, whereas ethyl cyanopropionylacetate yields a mixture of malonic and propionic acids.

*Ethyl Methylglutazinecarboxylate*,  $\text{NH} \begin{array}{c} \text{CO} \text{---} \text{CHMe} \\ \text{CO} \cdot \text{CH}(\text{CO}_2\text{Et}) \end{array} \text{C:NH}.$

Eight grams of ethyl  $\beta$ -imino- $\alpha$ -cyano- $\alpha'$ -methylglutarate were dissolved in cold concentrated sulphuric acid and the well-cooled solution left for 10 minutes; on pouring into water, a copious, white precipitate was formed, which was collected and recrystallised from glacial acetic acid.

Ethyl methylglutazinecarboxylate consists of large needles, which melt and decompose at  $213^\circ$  and which give in dilute alcoholic solution a deep purple coloration with ferric chloride, disappearing on heating.

0.1874 gave 0.3487  $\text{CO}_2$  and 0.1014  $\text{H}_2\text{O}$ .  $\text{C} = 50.76$ ;  $\text{H} = 6.01$ .

$\text{C}_9\text{H}_{12}\text{O}_4\text{N}_2$  requires  $\text{C} = 50.9$ ;  $\text{H} = 5.7$  per cent.

This substance is not soluble in cold alkalis, but readily dissolves on warming; it is very soluble in cold mineral acids. The *dibenzoyl* derivative, prepared in the usual way, crystallises from absolute alcohol in the form of small needles and melts at  $210^\circ$ .

0.2002 gave 0.4803  $\text{CO}_2$  and 0.776  $\text{H}_2\text{O}$ .  $\text{C} = 65.43$ ;  $\text{H} = 4.31$ .

$\text{C}_{23}\text{H}_{19}\text{O}_6\text{N}_2$  requires  $\text{C} = 65.8$ ;  $\text{H} = 4.5$  per cent.

When the carefully dried and purified ethyl hydrogen  $\beta$ -imino- $\alpha$ -cyano- $\alpha'$ -methylglutarate,  $\text{CO}_2\text{H} \cdot \text{CHMe} \cdot \text{C}(\text{NH}) \cdot \text{CH}(\text{CN}) \cdot \text{CO}_2\text{Et}$ , is heated for 5—10 minutes at  $147^\circ$ , that is, at a few degrees above its melting point, no appreciable amount of carbon dioxide is eliminated, but the melted compound slowly solidifies. The product on investigation proved to be a mixture of a small quantity of ethyl  $\beta$ -imino- $\alpha$ -cyanovalerate with ethyl methylglutazinecarboxylate; these were separated by treatment with hot absolute alcohol, in which the former is readily soluble.

*Ethyl 2 : 4 : 6-Trioxypyridine-5-methyl-3-carboxylate*,



When a solution of ethyl methylglutazinecarboxylate in caustic soda is mixed with an aqueous solution of sodium nitrite and the mixture poured into acetic acid, a considerable quantity of nitrogen is evolved, and the solution becomes dark green; after evaporating, the pyridine derivative slowly separates and can be recrystallised from dilute acetic acid. It melts and decomposes at a high temperature, and gives in dilute alcoholic solution a red coloration with ferric chloride; it is soluble in acids and alkalis.

0.1927 gave 0.3567  $\text{CO}_2$  and 0.0869  $\text{H}_2\text{O}$ .  $\text{C} = 50.48$ ;  $\text{H} = 5.01$ .

$\text{C}_9\text{H}_{11}\text{O}_5\text{N}$  requires  $\text{C} = 50.7$ ;  $\text{H} = 5.1$  per cent.

2 : 4 : 6-*Trioxo-5-methylpyridine*,  $\text{NH} \begin{smallmatrix} \text{CO} \cdot \text{CHMe} \\ \text{CO} - \text{CH}_2 \end{smallmatrix} \text{CO}$ , is prepared from the ethyl salt of its carboxylic acid by boiling it for a short time with aqueous caustic potash. On acidifying with hydrochloric acid and evaporating to dryness, the hydrochloride can be extracted from the residue by means of alcohol, and the free base derived from this on treating it with the calculated quantity of sodium hydroxide solution. It crystallises from a little water, in which it is fairly soluble in the cold, in the form of microscopic prisms, which, in aqueous solution, give a deep red coloration with ferric chloride. It melts at about  $240^\circ$  with evolution of gas.

0.2104 gave 0.3942  $\text{CO}_2$  and 0.0896  $\text{H}_2\text{O}$ .  $\text{C} = 51.12$ ;  $\text{H} = 4.73$ .

$\text{C}_6\text{H}_7\text{O}_3\text{N}$  requires  $\text{C} = 51.1$ ;  $\text{H} = 4.9$  per cent.

*Preparation of Methylglutazine*,  $\text{NH} \begin{smallmatrix} \text{CO} \cdot \text{CHMe} \\ \text{CO} - \text{CH}_2 \end{smallmatrix} \text{C} \cdot \text{NH}$ , from *Ethyl Methylglutazinecarboxylate*.

The ethyl salt dissolves in a large excess of sodium hydroxide solution, but a sodium salt is slowly deposited. This, however, dissolves when boiled, and if the heating be continued in a wide-mouthed tube until ammonia begins to be evolved, the residue, on acidifying with acetic acid, will give a crystalline precipitate of methylglutazine.

As in the case of glutazine itself, however, the solution has to be nearly evaporated to dryness before the hydrolysis is complete. Methylglutazine separates from water in needles, which have usually a bright red colour; it melts about  $260^\circ$  and gives in aqueous solution a red coloration with ferric chloride, which disappears again almost instantly.

0.2084 gave 0.3913  $\text{CO}_2$  and 0.1115  $\text{H}_2\text{O}$ .  $\text{C} = 51.22$ ;  $\text{H} = 5.94$ .

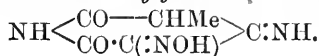
$\text{C}_6\text{H}_8\text{O}_2\text{N}_2$  requires  $\text{C} = 51.4$ ;  $\text{H} = 5.7$  per cent.

The *hydrochloride* separates in fine needles from concentrated hydrochloric acid; it is unstable in the presence of water. The *dibenzoyl* derivative, prepared from benzoyl chloride and methylglutazine, separates from hot glacial acetic acid in small plates which melt at  $214^\circ$ .

0.1690 gave 0.4259  $\text{CO}_2$  and 0.0717  $\text{H}_2\text{O}$ .  $\text{C} = 68.73$ ;  $\text{H} = 4.72$ .

$\text{C}_6\text{H}_7\text{O}_3\text{N}_3$  requires  $\text{C} = 69.0$ ;  $\text{H} = 4.6$  per cent.

*Action of Nitrous Acid on Methylglutazine. Formation of the Oxime,*



This substance was prepared in the manner previously described, namely, by dissolving methylglutazine in water, adding caustic soda and sodium nitrite solution, and pouring the mixture into dilute acetic acid. A deep red solution is formed, which gradually deposits a red, crystalline substance containing sodium. When treated with dilute hydrochloric acid, this product is transformed into the free acid, which can be obtained in yellowish-white crystals from a large quantity of water.

Neither the sodium salt nor the free acid gives the Liebermann reaction, and the former, or the latter when neutralised, gives a deep green coloration with ferrous sulphate. Solutions of the free acid are reddened with alkalis.

0.1224 gave 0.1919  $\text{CO}_2$  and 0.0422  $\text{H}_2\text{O}$ .  $\text{C} = 42.76$  ;  $\text{H} = 3.83$ .

$\text{C}_6\text{H}_7\text{O}_3\text{N}_3$  requires  $\text{C} = 42.6$  ;  $\text{H} = 4.14$  per cent.

Prolonged boiling with concentrated hydrochloric or dilute (1:4) sulphuric acid fails to hydrolyse methylglutazine to the corresponding pyridine derivative, and in each case the methyl base was recovered unchanged. Hence by the action of dilute sulphuric or hydrochloric acid on ethyl  $\beta$ -imino- $\alpha$ -cyano- $\alpha'$ -methylglutarate, methylglutazine only is produced.

*Ethyl  $\beta$ -imino- $\alpha$ -cyano- $\alpha'$ -dimethylglutarate,*  
 $\text{CO}_2\text{Et} \cdot \text{CHMe} \cdot \text{C}(\text{:NH}) \cdot \text{CMe}(\text{CN}) \cdot \text{CO}_2\text{Et}.$

The preparation of this substance was effected in two ways.

I. From the sodium derivative of ethyl  $\beta$ -imino- $\alpha$ -cyano- $\alpha'$ -methylglutarate and methyl iodide:

Ethyl  $\beta$ -imino- $\alpha$ -cyano- $\alpha'$ -methylglutarate (17.5 grams) was heated with a solution containing 1.7 grams of sodium dissolved in alcohol and excess of methyl iodide immediately added; after heating for from 4 to 5 hours, water was added and the precipitated oil extracted by ether. On fractionation, the larger portion distilled at  $200-225^\circ/25$  mm., and slowly deposited crystals, which proved to be this dimethyl compound, and after recrystallisation from dilute alcohol formed small needles, melted at  $64^\circ$ , and boiled at  $215^\circ/22$  mm. pressure.

0.1407 gave 0.2913  $\text{CO}_2$  and 0.0914  $\text{H}_2\text{O}$ .  $\text{C} = 56.47$  ;  $\text{H} = 7.2$ .

$\text{C}_{12}\text{H}_{18}\text{O}_4\text{N}_2$  requires  $\text{C} = 56.7$  ;  $\text{H} = 7.1$  per cent.

II. From the condensation of ethyl cyanomethylacetate with its sodium derivative:

Two molecular proportions of ethyl cyanomethylacetate were heated on the water-bath with 1 molecule of sodium dissolved in alcohol. At the end of 5 hours, the dark brown product was poured into dilute hydrochloric acid, and the oil which separated extracted with ether. Only a small yield of a high boiling oil was obtained on fractionation, which passed over at  $215^{\circ}/22$  mm., and, on cooling, solidified to crystals which separated from dilute alcohol in small prisms and melted at  $64^{\circ}$ . The yield of the substance is not more than 20 per cent. of the theory. A comparison of its properties with those of the compound prepared by the first method proved the two to be identical.

0.3008 gave 0.6435  $\text{CO}_2$  and 0.1940  $\text{H}_2\text{O}$ .  $\text{C} = 56.81$ ;  $\text{H} = 7.00$ .

$\text{C}_{12}\text{H}_{18}\text{O}_4\text{N}_2$  requires  $\text{C} = 56.7$ ;  $\text{H} = 7.1$  per cent.

*Formation of Ethyl  $\beta$ -Imino- $\alpha$ -cyano- $\alpha$ -methylvalerate,*  
 $\text{EtC}(\text{NH})\cdot\text{CMe}(\text{CN})\cdot\text{CO}_2\text{Et}$ .

Ethyl  $\beta$ -imino- $\alpha$ -cyano- $\alpha\alpha'$ -dimethylglutarate does not readily dissolve in 30 per cent. aqueous sodium carbonate, and prolonged boiling is necessary before complete solution is effected. On cooling, a considerable quantity of the above compound crystallises out; when recrystallised from absolute alcohol, it forms small needles which melt at  $119^{\circ}$ .

0.2157 gave 0.5457  $\text{CO}_2$  and 0.1737  $\text{H}_2\text{O}$ .  $\text{C} = 59.13$ ;  $\text{H} = 7.67$ .

$\text{C}_9\text{H}_{14}\text{O}_2\text{N}_2$  requires  $\text{C} = 59.3$ ;  $\text{H} = 7.7$  per cent.

On acidifying the sodium carbonate mother liquors, no precipitate of the ethyl hydrogen salt took place, and, therefore, under the conditions of the experiment, the whole of the ethyl  $\beta$ -imino- $\alpha$ -cyano- $\alpha\alpha'$ -dimethylglutarate had been converted into ethyl  $\beta$ -imino- $\alpha$ -cyano- $\alpha$ -methylvalerate.

*Action of Dilute Sulphuric Acid on Ethyl  $\beta$ -Imino- $\alpha$ -cyano- $\alpha$ -methylvalerate. Formation of Ethyl Cyanopropionylmethylacetate,*  
 $\text{EtCO}\cdot\text{CMe}(\text{CN})\cdot\text{CO}_2\text{Et}$ .

This substance was prepared by boiling the ethyl salt with dilute (1:4) sulphuric acid, at the same time passing a current of steam through the hydrolysing solution; it passes over with the steam, and can be extracted from the distillate by means of ether. It is a mobile oil boiling at  $230$ — $235^{\circ}$  under the ordinary pressure.

0.2137 gave 0.4606  $\text{CO}_2$  and 0.1391  $\text{H}_2\text{O}$ .  $\text{C} = 58.79$ ;  $\text{H} = 7.23$ .

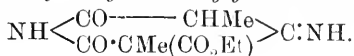
$\text{C}_9\text{H}_{13}\text{O}_3\text{N}$  requires  $\text{C} = 59.0$ ;  $\text{H} = 7.1$  per cent.

Ethyl  $\beta$ -imino- $\alpha$ -cyano- $\alpha\alpha'$ -dimethylglutarate dissolves on boiling with strong caustic potash solution, and if, after ammonia has ceased to be evolved, the product is acidified, saturated with ammonium sulphate, and extracted with ether, methylmalonic acid (m. p.  $130^\circ$ ) is obtained as sole product.

0.2013 gave 0.2991  $\text{CO}_2$  and 0.0906  $\text{H}_2\text{O}$ .  $\text{C} = 40.52$ ;  $\text{H} = 5.00$ .

$\text{C}_4\text{H}_6\text{O}_4$  requires  $\text{C} = 40.7$ ;  $\text{H} = 5.1$  per cent.

*Formation of Ethyl Dimethylglutazincarboxylate,*



Ethyl  $\beta$ -imino- $\alpha$ -cyano- $\alpha\alpha'$ -dimethylglutarate dissolves readily in twice its volume of concentrated sulphuric acid, and if after 5 hours the solution is poured into water, a large quantity of the above compound is precipitated on partially neutralising. The yield is about 50 per cent. of the theory, the filtrate furnishing methylmalonic acid. Ethyl dimethylglutazincarboxylate crystallises from glacial acetic acid in small, colourless leaflets, which melt and decompose at  $225^\circ$ . It is appreciably soluble in hot water and dissolves in a mixture of one part of water to one part of alcohol; its neutral solutions give a deep violet colour with ferric chloride. It is insoluble in cold alkalis, but dissolves on warming; with acids it forms salts which are dissociated by water.

0.2213 gave 0.4293  $\text{CO}_2$  and 0.1219  $\text{H}_2\text{O}$ .  $\text{C} = 52.91$ ;  $\text{H} = 6.12$ .

$\text{C}_{10}\text{H}_{14}\text{O}_4\text{N}_2$  requires  $\text{C} = 53.1$ ;  $\text{H} = 6.2$  per cent.

The *hydrochloride* separates from concentrated hydrochloric acid in small, transparent prisms.

The *dibenzoyl* derivative is prepared by boiling the ethyl salt with benzoyl chloride until the evolution of hydrogen chloride ceases; it separates on cooling, and can be crystallised from glacial acetic acid, when it is obtained in small prisms which melt at  $235^\circ$ .

0.2122 gave 0.5137  $\text{CO}_2$  and 0.1003  $\text{H}_2\text{O}$ .  $\text{C} = 66.09$ ;  $\text{H} = 5.26$ .

$\text{C}_{24}\text{H}_{22}\text{O}_6\text{N}_2$  requires  $\text{C} = 66.3$ ;  $\text{H} = 5.1$  per cent.

No definite products were isolated when ethyl dimethylglutazincarboxylate was treated with nitrous acid, the majority of the ethyl salt being recovered unaltered.



This base can be prepared by heating the foregoing ethyl salt with strong potassium hydroxide solution in a wide-mouthed tube until the odour of ammonia becomes apparent. In this case also it is necessary to evaporate the solution until nearly all the water has been driven off before complete hydrolysis is effected. On acidifying with acetic acid, dimethylglutazine separates, and can be recrystallised from water forming yellow plates, which melt at a high temperature. It gives in aqueous solution a permanent red colour with ferric chloride.

0.2128 gave 0.4238  $\text{CO}_2$  and 0.1228  $\text{H}_2\text{O}$ .  $\text{C} = 54.32$ ;  $\text{H} = 6.42$ .

$\text{C}_7\text{H}_{10}\text{O}_2\text{N}_2$  requires  $\text{C} = 54.5$ ;  $\text{H} = 6.5$  per cent.

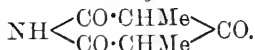
The yield of this substance is small, a quantity of methylmalonic acid being recovered from the filtrate.

The *dibenzoyl* derivative is prepared by boiling dimethylglutazine with benzoyl chloride until hydrogen chloride ceases to be evolved; it crystallises from the solution on cooling and when recrystallised from glacial acetic acid it forms small, glistening, yellow plates which melt at  $205^\circ$ .

0.2005 gave 0.5104  $\text{CO}_2$  and 0.0897  $\text{H}_2\text{O}$ .  $\text{C} = 69.43$ ;  $\text{H} = 4.97$ .

$\text{C}_{21}\text{H}_{15}\text{O}_4\text{N}_2$  requires  $\text{C} = 69.6$ ;  $\text{H} = 5.0$  per cent.

*Formation of 2:4:6-Trioxypyridine-3:5-dimethylpyridine,*



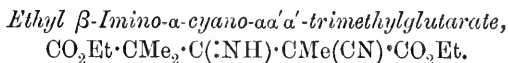
This substance was prepared by dissolving dimethylglutazine in a little alkali, adding a solution of the requisite quantity of sodium nitrite, and pouring the mixture into dilute acetic acid; a considerable quantity of nitrogen was evolved, and as no crystalline compound separated, the solution was therefore evaporated to dryness, hydrochloric acid being added and again evaporated. The solid residue was then extracted with alcohol, which dissolved out the hydrochloride of the above pyridine derivative. This was transformed into the free base by dissolving it in a little water and adding a solution of the calculated quantity of sodium hydroxide, when the trioxypyridine separated in the form of a brown precipitate. When recrystallised from water, it forms slender needles which are usually slightly coloured, and which give in aqueous solution a red coloration with ferric chloride.

0.1911 gave 0.3778  $\text{CO}_2$  and 0.0944  $\text{H}_2\text{O}$ .  $\text{C} = 53.92$ ;  $\text{H} = 5.49$ .

$\text{C}_7\text{H}_9\text{O}_3\text{N}$  requires  $\text{C} = 54.2$ ;  $\text{H} = 5.8$  per cent.

Prolonged action of concentrated hydrochloric acid or dilute (1 : 4) sulphuric acid does not hydrolyse dimethylglutazine to the corresponding pyridine derivatives.

On prolonged boiling of ethyl  $\beta$ -imino- $\alpha$ -cyano- $\alpha\alpha'$ -dimethylglutarate with dilute mineral acids, dimethylglutazine is the sole product.



This substance may be prepared by two methods :

I. Treatment of ethyl  $\beta$ -imino- $\alpha$ -cyanoglutarate with sodium ethoxide and methyl iodide. In order to obtain a pure product by this method, it is necessary to repeat the process three times, on each occasion using an excess of sodium ethoxide and methyl iodide, since the introduction of the last methyl group seems to take place with some difficulty. The ultimate product boils at  $200^\circ/30$  mm. and sets to a solid mass on cooling ; when recrystallised from dilute alcohol, it is obtained in small prisms melting at  $113^\circ$ .

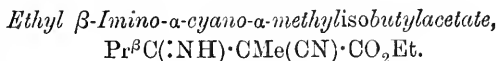
0.1927 gave 0.4099  $\text{CO}_2$  and 0.1252  $\text{H}_2\text{O}$ .  $\text{C} = 58.01$  ;  $\text{H} = 7.22$ .

$\text{C}_{13}\text{H}_{20}\text{O}_4\text{N}_2$  requires  $\text{C} = 58.2$  ;  $\text{H} = 7.4$  per cent.

II. By the action of methyl iodide on the sodium compound formed in the condensation of ethyl cyanomethylacetate with its sodium derivative. In this case, the product of the condensation, prepared as described on page 1736, was treated with excess of methyl iodide and boiled on the water-bath until the gelatinous sodium compound had completely dissolved. Water was then added and the oil which separated extracted with ether. The boiling and melting points of the substances were found to be the same as those given above.

0.2013 gave 0.4276  $\text{CO}_2$  and 0.1324  $\text{H}_2\text{O}$ .  $\text{C} = 57.93$  ;  $\text{H} = 7.31$ .

$\text{C}_{13}\text{H}_{20}\text{O}_4\text{N}_2$  requires  $\text{C} = 58.2$  ;  $\text{H} = 7.4$  per cent.



Ethyl  $\beta$ -imino- $\alpha$ -cyano- $\alpha\alpha'$ -trimethylglutarate only dissolves in a 30 per cent. aqueous sodium carbonate after prolonged boiling, and when all has dissolved the solution on cooling deposits the above compound. It crystallises from absolute alcohol in large, transparent prisms which melt at  $135^\circ$ .

0.2091 gave 0.4686  $\text{CO}_2$  and 0.1507  $\text{H}_2\text{O}$ .  $\text{C} = 61.12$  ;  $\text{H} = 8.01$ .

$\text{C}_{10}\text{H}_{16}\text{O}_2\text{N}_2$  requires  $\text{C} = 61.2$  ;  $\text{H} = 8.2$  per cent.

On acidifying the sodium carbonate mother liquors, no ethyl hydrogen salt was precipitated, the conditions of the experiment being such that only the above compound was formed.

*Ethyl Cyanoisobutyrylmethylacetate*,  $\text{Pr}^\beta\text{CO}\cdot\text{CMe}(\text{CN})\cdot\text{CO}_2\text{Et}$ .

The conditions of the experiment were the same as those indicated in the previous cases.

The ethyl salt was boiled with dilute (1 : 4) sulphuric acid and a current of steam passed through the hydrolysing mixture. Ethyl cyanoisobutyrylmethylacetate, which passed over with the steam and was extracted from the distillate by means of ether, is a mobile liquid boiling at  $240^\circ$  under the ordinary pressure.

0.2125 gave 0.4732  $\text{CO}_2$  and 0.1419  $\text{H}_2\text{O}$ .  $\text{C} = 60.73$ ;  $\text{H} = 7.42$ .

$\text{C}_{10}\text{H}_{15}\text{O}_3\text{N}$  requires  $\text{C} = 60.9$ ;  $\text{H} = 7.6$  per cent.

Ethyl  $\beta$ -imino- $\alpha$ -cyano- $\alpha\alpha'$ -trimethylglutarate dissolves slowly on boiling in aqueous sodium hydroxide, and if the heating is continued until no more ammonia is evolved, the solution, on acidifying, saturating with ammonium sulphate, and extracting with ether, yields a solid which was found to consist of a mixture of methylmalonic and dimethylmalonic acids. These acids were separated by recrystallisation from concentrated hydrochloric acid, from which solvent dimethylmalonic acid crystallises, leaving methylmalonic acid in solution.

Three recrystallisations sufficed to cause the former acid to show the correct melting point ( $185^\circ$ ).

0.2129 gave 0.3529  $\text{CO}_2$  and 0.1153  $\text{H}_2\text{O}$ .  $\text{C} = 45.21$ ;  $\text{H} = 6.02$ .

$\text{C}_5\text{H}_8\text{O}_4$  requires  $\text{C} = 45.4$ ;  $\text{H} = 6.1$  per cent.

The methylmalonic acid was extracted from the mother liquors and found to melt at  $130^\circ$ .

When ethyl  $\beta$ -amino- $\alpha$ -cyano- $\alpha\alpha'$ -trimethylglutarate is dissolved in cold concentrated sulphuric acid, and the solution, after 2 hours, is poured into water, no precipitation takes place, but the solution smells strongly of isobutyric acid.

When neutralised with ammonia and again acidified with hydrochloric acid, the solution gave, on extraction with ether, a crystalline substance which proved to be a mixture of methylmalonic and dimethylmalonic acids.

Evidently, therefore, the glutazine derivative is not formed from ethyl  $\beta$ -imino- $\alpha$ -cyano- $\alpha\alpha'$ -trimethylglutarate under these conditions, the ethyl salt breaking down into straight chain degradation products.

*Ethyl β-Imino-α-cyano-α'-ethylglutarate,*  
 $\text{CO}_2\text{Et} \cdot \text{CHEt} \cdot \text{C}(\text{:NH}) \cdot \text{CH}(\text{CN}) \cdot \text{CO}_2\text{Et}.$

If the gelatinous sodium compound produced in the condensation of ethyl cyanoacetate with its sodium derivative is treated with excess of ethyl iodide and heated on the water-bath until the sodium compound has dissolved, the above ethyl salt is obtained on adding water, extracting with ether, and fractionating. It boils at  $215^\circ/20$  mm. and crystallises from dilute alcohol in prisms which melt at  $68^\circ$ .

0.2019 gave 0.4183  $\text{CO}_2$  and 0.1275  $\text{H}_2\text{O}$ .  $\text{C} = 56.51$ ;  $\text{H} = 7.02$ .

$\text{C}_{12}\text{H}_{18}\text{O}_4\text{N}_2$  requires  $\text{C} = 56.7$ ;  $\text{H} = 7.1$  per cent.

*Ethyl β-Imino-α-cyano-η-caprolate, Pr<sup>a</sup>C(:NH)·CH(CN)·CO<sub>2</sub>Et, and*  
*Ethyl Hydrogen β-Imino-α-cyano α'-ethylglutarate,*  
 $\text{CO}_2\text{H} \cdot \text{CHEt} \cdot \text{C}(\text{:NH}) \cdot \text{CH}(\text{CN}) \cdot \text{CO}_2\text{Et}.$

Ethyl β-imino-α-cyano-α'-ethylglutarate does not readily dissolve in 30 per cent. aqueous sodium carbonate, and it is necessary to boil for some time before complete solution is effected. On cooling, a crystalline substance separates, which was found to be ethyl β-imino-α-cyano-η-caprolate. It separates from absolute alcohol in small plates which melt at  $115^\circ$ .

0.2199 gave 0.4774  $\text{CO}_2$  and 0.1488  $\text{H}_2\text{O}$ .  $\text{C} = 59.21$ ;  $\text{H} = 7.52$ .

$\text{C}_9\text{H}_{14}\text{O}_2\text{N}_2$  requires  $\text{C} = 59.3$ ;  $\text{H} = 7.7$  per cent.

On acidifying the sodium carbonate solution, a quantity of crystals separated. These were collected and found to consist of ethyl hydrogen β-imino-α-cyano-α'-ethylglutarate. When recrystallised from hot water, this substance forms transparent prisms which melt at  $153^\circ$ , giving off carbon dioxide at  $170^\circ$ , and between these temperatures being converted into ethyl ethylglutazinecarboxylate.

0.2357 gave 0.4573  $\text{CO}_2$  and 0.1308  $\text{H}_2\text{O}$ .  $\text{C} = 52.92$ ;  $\text{H} = 6.17$ .

$\text{C}_{10}\text{H}_{14}\text{O}_4\text{N}_2$  requires  $\text{C} = 53.1$ ;  $\text{H} = 6.2$  per cent.

*Ethyl Cyanobutyrylacetate, Pr<sup>a</sup>CO·CH(CN)·CO<sub>2</sub>Et.*

When ethyl β-imino-α-cyano-η-caprolate is boiled with dilute sulphuric acid and steam is passed through the solution, the above compound passes over with the steam, and can be extracted with ether from the aqueous distillate. It is a mobile liquid, boiling at  $235^\circ$  under the ordinary pressure.

0.2009 gave 0.4326  $\text{CO}_2$  and 0.1269  $\text{H}_2\text{O}$ .  $\text{C} = 58.73$ ;  $\text{H} = 7.02$ .

$\text{C}_9\text{H}_{13}\text{O}_3\text{N}$  requires  $\text{C} = 59.0$ ;  $\text{H} = 7.1$  per cent.

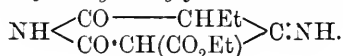
Ethyl  $\beta$ -imino- $\alpha$ -cyano- $\alpha'$ -ethylglutarate dissolves on boiling with aqueous caustic soda, and if the heating is continued until ammonia ceases to be evolved, the product, on acidifying, saturating with ammonium sulphate, and extracting, yields ethylmalonic acid, crystallising from concentrated hydrochloric acid in small plates which melt at  $112^\circ$ .

0.1799 gave 0.2982  $\text{CO}_2$  and 0.0976  $\text{H}_2\text{O}$ .  $\text{C} = 45.21$ ;  $\text{H} = 6.03$ .

$\text{C}_5\text{H}_8\text{O}_4$  requires  $\text{C} = 45.4$ ;  $\text{H} = 6.1$  per cent.

Malonic acid (m. p.  $132^\circ$ ) was obtained from the mother liquors on evaporating to dryness and extracting with ether in a Soxhlet apparatus.

*Formation of Ethyl Ethylglutazinecarboxylate,*



This compound is best prepared by dissolving the ethyl salt in twice its volume of concentrated sulphuric acid and leaving the mixture for 12 hours. On pouring into water, no precipitation of the base immediately takes place owing to the stability of its sulphate; if, however, ammonia is cautiously added, a white precipitate is produced.

When recrystallised from glacial acetic acid, ethyl glutazinecarboxylate forms small, colourless prisms, which melt at  $212^\circ$  to a red liquid. It is soluble in caustic potash solution in the cold, from which a bulky potassium salt slowly separates. It also dissolves in hot concentrated hydrochloric acid, and the solution on cooling deposits the hydrochloride in the form of small, colourless prisms.

Ethyl ethylglutazinecarboxylate gives in alcoholic solution a greenish-blue coloration with ferric chloride.

0.1566 gave 0.3076  $\text{CO}_2$  and 0.0954  $\text{H}_2\text{O}$ .  $\text{C} = 53.57$ ;  $\text{H} = 6.13$ .

0.1207 „ 14 c.c. nitrogen at  $20^\circ$  and 757 mm.  $\text{N} = 12.7$ .

$\text{C}_{10}\text{H}_{14}\text{O}_4\text{N}_2$  requires  $\text{C} = 53.1$ ;  $\text{H} = 6.2$ ;  $\text{N} = 12.4$  per cent.

The *dibenzoyl* derivative, prepared in the usual way, separates from glacial acetic acid in lustrous plates which melt at  $229^\circ$ .

0.1725 gave 0.1488  $\text{CO}_2$  and 0.0763  $\text{H}_2\text{O}$ .  $\text{C} = 66.21$ ;  $\text{H} = 4.91$ .

$\text{C}_{24}\text{H}_{22}\text{O}_6\text{N}_2$  requires  $\text{C} = 66.3$ ;  $\text{H} = 5.1$  per cent.

In one experiment, the sulphuric acid solution, when left for only 3 hours, was poured into water and the mixture allowed to get hot; on cooling and partially neutralising with ammonia, a white precipitate separated, which was found to consist of ethyl ethylglutazine-

carboxylate and another substance. The latter was extracted by means of warm absolute alcohol and recrystallised by dilute alcohol. In this way, it was obtained in the form of long, slender needles which melted at  $83^{\circ}$ . It proved to be an acid soluble in sodium carbonate solution with effervescence, and analysis showed that it had the formula  $C_9H_{15}O_4N$ .

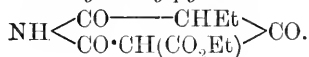
0.1428 gave 0.2821  $CO_2$  and 0.1007  $H_2O$ .  $C = 53.88$ ;  $H = 7.83$ .

0.1803 „ 0.3538  $CO_2$  „ 0.1236  $H_2O$ .  $C = 53.52$ ;  $H = 7.61$ .

$C_9H_{15}O_4N$  requires  $C = 53.7$ ;  $H = 7.5$  per cent.

In all probability this substance is *ethyl hydrogen  $\beta$ -imino- $\alpha'$ -ethylglutarate*,  $CO_2Et \cdot CHEt \cdot C(:NH) \cdot CH_2 \cdot CO_2H$ .

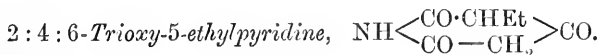
*Ethyl 2 : 4 : 6-Trioxo-5-ethylpyridine-3-carboxylate*,



When a solution of ethyl ethylglutazincarboxylate dissolved in warm aqueous caustic soda is mixed with a solution containing the calculated quantity of sodium nitrite and the mixture poured into dilute acetic acid, a considerable volume of nitrogen is evolved and the dark green solution slowly deposits crystals of the above substance. The product crystallises from absolute alcohol in the form of small prisms which melt above  $260^{\circ}$  and give in alcoholic solution a deep purple coloration with ferric chloride. It is soluble both in acids and alkalis.

0.2001 gave 0.3869  $CO_2$  and 0.1010  $H_2O$ .  $C = 52.73$ ;  $H = 5.61$ .

$C_{10}H_{13}O_5N$  requires  $C = 52.9$ ;  $H = 5.7$  per cent.



This base is prepared by the hydrolysis of the preceding ethyl salt with aqueous caustic potash. After boiling for 2 hours, the dark product was acidified with hydrochloric acid and evaporated to dryness, the residue being extracted with alcohol.

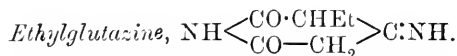
The hydrochloride of 2 : 4 : 6-trioxo-5-ethylpyridine dissolves in the alcohol and can be recovered on evaporation. It was then dissolved in water and the calculated quantity of sodium carbonate solution added, when the base separated as a brown, crystalline precipitate. When recrystallised from water, in which it is fairly soluble, the base is obtained in the form of pale yellow leaflets which melt and decompose at about  $245^{\circ}$  and give in aqueous solution a reddish-violet coloration with ferric chloride.

0.1992 gave 0.3945 CO<sub>2</sub> and 0.1006 H<sub>2</sub>O. C = 54.02; H = 5.61.

C<sub>7</sub>H<sub>9</sub>O<sub>3</sub>N requires C = 54.2; H = 5.8 per cent.

*Conversion of Ethyl Hydrogen β-Imino-α-cyano-α'-ethylglutarate into Ethyl Ethylglutazinecarboxylate.*

This conversion is brought about by heating the carefully dried and powdered ethyl hydrogen salt at 155° for from 10 to 15 minutes. The substance first melts and gives off a small quantity of gas; it then resolidifies to a yellow mass. When extracted with absolute alcohol, this product proved to be a mixture of a small quantity of ethyl β-imino-α-cyano-*n*-caprolate with ethyl ethylglutazinecarboxylate, the latter being present to the extent of about 80 per cent.



This substance is prepared by heating ethyl ethylglutazinecarboxylate with strong caustic potash solution and boiling in a wide-mouthed tube until the odour of ammonia becomes apparent. On acidifying with acetic acid, ethylglutazine separates and can be collected and recrystallised from water. In this way it is obtained in the form of lemon-yellow plates which melt at about 260° and give in aqueous solution a red coloration with ferric chloride.

0.1954 gave 0.3012 CO<sub>2</sub> and 0.1174 H<sub>2</sub>O. C = 54.62; H = 6.67.

C<sub>7</sub>H<sub>10</sub>O<sub>2</sub>N<sub>2</sub> requires C = 54.55; H = 6.5 per cent.

The *dibenzoyl* derivative, prepared in the usual way, crystallises from glacial acetic acid in the form of glistening plates which melt at 209°.

0.2017 gave 0.5130 CO<sub>2</sub> and 0.0875 H<sub>2</sub>O. C = 69.37; H = 4.82.

C<sub>21</sub>H<sub>18</sub>O<sub>4</sub>N<sub>2</sub> requires C = 69.6; H = 5.0 per cent.

The *oxime*, NH  $\begin{array}{c} \text{CO} - \text{CHEt} \\ \text{CO} \cdot \text{C}(:\text{NOH}) \end{array} > \text{C} : \text{NH}$ , is prepared by mixing an aqueous solution of ethylglutazine with an aqueous solution of sodium nitrite and pouring the mixture into a 50 per cent. solution of acetic acid. The solution at first becomes red, but gradually changes to yellow, and slowly deposits a yellow, crystalline compound.

This substance, which is the free oxime, crystallises from dilute alcohol in small, light yellow needles, dissolving in alkali to form a red solution which, when neutral, gives a deep bluish-green coloration with ferrous sulphate.

0.1921 gave 0.3214 CO<sub>2</sub> and 0.0816 H<sub>2</sub>O. C = 45.63; H = 4.72.

C<sub>7</sub>H<sub>9</sub>O<sub>3</sub>N<sub>3</sub> requires C = 45.9; H = 4.9 per cent.

Strong mineral acids are, under the ordinary conditions, without action on ethylglutazine, and we have been unable as yet to prepare the corresponding trioxypyridine derivative in this way.

Experiments having for their object the preparation and investigation of these substances are in progress, as well as the study of similar condensation products formed by the interaction of ethyl cyanoacetate and other compounds containing negative hydrogen atoms.

Much of the expense entailed in this research has been met by a grant from the Research Fund of the Chemical Society, for which we desire to express our indebtedness.

CHEMICAL LABORATORY,  
THE UNIVERSITY,  
MANCHESTER.

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## ERRATA.

### VOL. LXIX (TRANS., 1896).

Page	Line	
988	2	for " $C_{17}H_{20}O_2$ " read " $C_{15}H_{16}O_2$ ."

### VOL. LXXIX (TRANS., 1901).

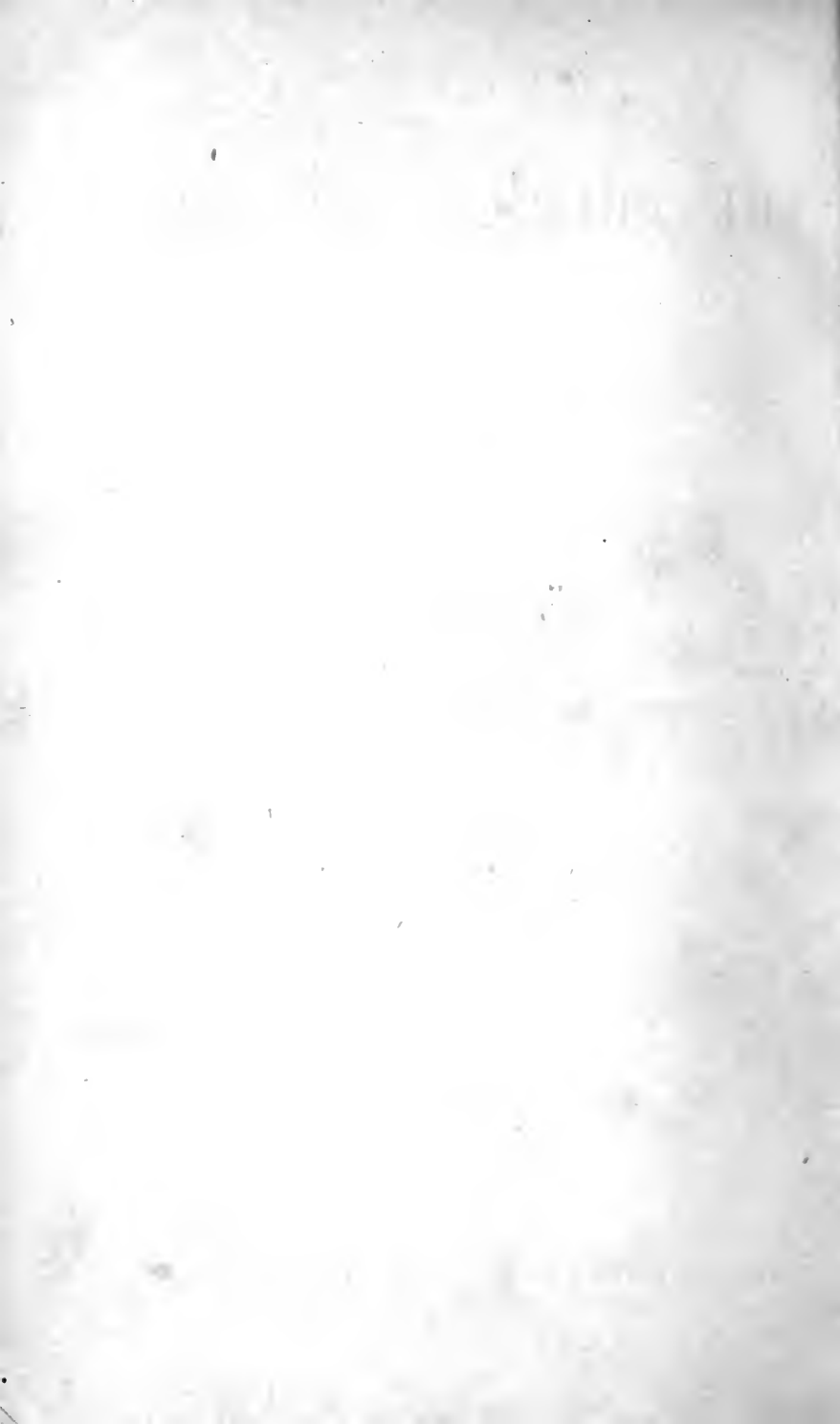
1209	4	for " $C=81.65$ ; $H=8.87$ " read " $C=81.17$ ; $H=9.41$ ."
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### VOL. LXXXV (TRANS., 1904).

267	1*	for "VI" read "VII."
267	2*	,, "VII" read "VIII."
273	13	delete "Ag haloids= $187.0$ ."
466	15*	for "The additive compound" read "Benzylideneaniline."
981	20	,, " $H_2SO_4$ " read " $NaOH$ ."
1236	2*	,, "solution" read "solutions."
1477	11	delete sentence "As both . . . ketones."
1496	17	for "2-acetyl-1:5-diphenyl-3-pyrazole" read "2-acetyl-1:5-diphenyl-3-pyrazolone."
1739	10*	,, " $C_{13}H_{17}O_5N_3$ " read " $C_{13}H_{17}O_3N_5$ ."

\* From bottom.













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